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VISCOSITY AND FLUIDITY.

[NINTH COMMUNICATION BEARING ON THIS SUBJECT.]

BY EUGENE C. BINGHAM.

In a recent paper[1] by the author it was shown that the simple formula,

$$t = A\varphi - B/\varphi + C,$$

can be used to represent fluidity data with an ease and accuracy unequalled by any formula heretofore proposed. This formula was derived from the fundamental assumption that, for the ideal liquid, fluidities are directly proportional to the absolute temperature. The following facts have led the author to the belief that the above hypothesis is now fairly substantiated.

1. This hypothesis admits of a simple physical explanation, as already pointed out,[2] on the basis of the kinetic theory. Fluidity and viscosity are the exact analogues of conductance and resistance, respectively, in electricity. The alternate hypothesis that viscosities are additive, which has been held until recently, does not permit of a simple physical conception.

[1] Bingham: Z. physik. Chem., **68**, 238 (1909). THIS JOURNAL, **40**, 277 (1908).
[2] Bingham: THIS JOURNAL, **35**, 195 (1906).

2. It has already been shown by many investigators[1] that there is, in fact, a parallelism between fluidity and conductivity. This would be unintelligible under the old assumption.

3. The fluidities of mixtures of liquids, where there is no marked temperature or volume change on mixing, are additive, as the hypothesis demands.[2]

4. The fluidities of unassociated liquids are, to a marked degree, directly proportional to the temperature. Even associated compounds appear to behave similarly at high temperatures.[3]

5. By comparing fluidities, instead of viscosities, new relations are brought out between fluidity and other physical properties. For example, the fluidities of all of the aliphatic hydrocarbons are nearly identical at their boiling points. The same is true for the ethers, and a simple relation exists between the fluidities of other classes, as iodides and bromides, at their boiling points. These relations do not make themselves evident when viscosities are compared, as has been done heretofore.

6. One of the most convincing arguments in favor of the hypothesis lies in the fact that the best results obtained in comparing viscosities have been at temperatures (or viscosities) of *equal slope*. This is precisely the same as comparing temperatures of equal fluidity *for a given class of compounds*, as I have shown.[4] But comparing temperatures (or viscosities) of equal slope on the viscosity curves does not give satisfactory results for *different classes* of compounds. Thus oxygen has a different value in each class. But when fluidities are compared the value of oxygen is the same in all classes of compounds. I believe that the same is true of the other atoms and groups. It seems to be something like a confession of ignorance of the property dealt with, when we assume a definite value for an atom or group and then find it necessary to change that value for every class of compounds.

[1] Jones and Bingham: Z. physik. Chem., **57**, 237 (1906). THIS JOURNAL, **34**, 547 (1905). Bingham: Diss., Johns Hopkins, 1905, p. 71.

[2] Bingham: THIS JOURNAL, **35**, 214 (1906).

[3] Bingham and Miss Harrison: Z. physik. Chem., **66**, 2 *et seq.* (1909).

[4] *Ibid.*, p. 19 *et seq.*

7. Furthermore, by comparing fluidities, it is possible to get a measure of association[1]—a thing which has never before been attempted, so far as is known to the author, by the analysis of viscosity data according to the older conception.

8. The fact that a simple equation, derived from the use of the above hypothesis, excels the equations heretofore proposed to represent viscosity data and that with a slight modification it will represent the observed values to nearly the limits of experimental error, is evidence in itself, and when taken in connection with the other facts mentioned above or to be found in the papers already referred to, it seems to make the evidence sufficiently strong to permit the provisional acceptance of the hypothesis, until facts arise which shall call it again into question and make worth while the search for further direct evidence. In the meantime it will be used for further investigation.

If the above view is correct, it is important that it become established as speedily as possible. For, as already pointed out, the view that viscosities are additive, which is still current, has led investigators to very erroneous conclusions. Moreover, it keeps viscosity (or its reciprocal, fluidity) from assuming its proper importance among the physical properties, the property being scarcely discussed in our text-books. Yet the laws of viscosity are doubtless fundamental in the understanding of conductivity in solution, ionic migration, diffusion, velocity of reaction, association; and viscosity is intimately connected with still other properties, such as vapor pressure and cubical expansion.

The author has already discussed some of these connections on the hypothesis that fluidities, *and not viscosities*, are additive. Others will be discussed in this and succeeding papers.

FLUIDITY FORMULAS.

In an early paper[2] I suggested the use, for the representation of viscosity data, of a formula of the form

$$\varphi = c/(\varphi - at - b),$$

[1] Bingham and Miss Harrison: Z. physik. Chem., **66**, 26 *et seq.* (1909).
[2] THIS JOURNAL, **35**, 216 (1906).

where φ represents fluidity, t temperature, and a, b, and c are constants. This formula was suggested to me in a conversation with Dr. A. B. Coble, of the Johns Hopkins University, while discussing the mathematical properties of a fluidity curve according to my hypothesis. Later, I derived the formula

$$t = A\varphi - B/\varphi + C,$$

which proved capable of representing viscosity data with fidelity, and the earlier formula was lost sight of. It is worth while to note, however, that both are reducible to the same form when $A = 1/a$, $B = c/a$, and $C = -b/a$.

Volume.

It is interesting to note that van der Waal's equation,

$$\left(p - \frac{a}{v^2}\right)(v - b) = RT,$$

gives

$$T = \frac{p}{R}v - \frac{pb}{R} - \frac{a}{Rv} + \frac{ab}{Rv^2},$$

which, when the pressure is constant, is the same as my simpler formula, with the exception of the amplifying term $\frac{ab}{Rv^2}$, and of the sign of the constant $\frac{pb}{R}$, which may be dependent upon the dimensions of the units employed. It would not be very surprising, perhaps, if some intimate relation could be established between volume and fluidity, and there is every reason why the question should be investigated. The above formula can easily be tested in the simpler form,

$$T = \alpha\varphi - \beta - \frac{\gamma}{\varphi} + \frac{\delta}{\varphi^2},$$

where α, β, γ, and δ are constants. This has been done for a number of substances to which my simple formula did not apply very well and also for octane. The result is shown in the following tables. The data used are those furnished by the viscosity observations of Thorpe and Rodger and

already used by me in testing my other formulas. To save space only the observed temperatures and those calculated by the formula are given, together with the percenatge differences.

The equations used in calculating the constants are the following:

$$\alpha = \frac{t_2 - t_1}{\varphi_2 - \varphi} - \frac{\gamma}{\varphi_1\varphi_2} + \frac{\delta(\varphi_1 + \varphi_2)}{\varphi_1^2\varphi_2^2}$$

$$\beta = t_1 + \frac{\gamma}{\varphi_1} - \frac{\delta}{\varphi_1^2} - \alpha\varphi_1$$

$$\gamma = \frac{\dfrac{t_3 - t_2}{\varphi_3 - \varphi_2} - \dfrac{t_2 - t_1}{\varphi_2 - \varphi_1} - \delta\left(\dfrac{\varphi_1 + \varphi_2}{\varphi_1^2\varphi_2^2} - \dfrac{\varphi_2 + \varphi_3}{\varphi_2^2\varphi_3^2}\right)}{\dfrac{1}{\varphi_2\varphi_3} - \dfrac{1}{\varphi_1\varphi_2}}$$

$$\delta = \frac{\left(\dfrac{t_3 - t_2}{\varphi_3 - \varphi_2} - \dfrac{t_4 - t_3}{\varphi_4 - \varphi_3}\right)\left(\dfrac{1}{\varphi_1\varphi_2} - \dfrac{1}{\varphi_2\varphi_3}\right) - \left(\dfrac{t_2 - t_1}{\varphi_2 - \varphi_1} - \dfrac{t_3 - t_2}{\varphi_3 - \varphi_2}\right)\left(\dfrac{1}{\varphi_2\varphi_3} - \dfrac{1}{\varphi_3\varphi_4}\right)}{\left(\dfrac{\varphi_1 + \varphi_2}{\varphi_1^2\varphi_2^2} - \dfrac{\varphi_2 + \varphi_3}{\varphi_2^2\varphi_3^2}\right)\left(\dfrac{1}{\varphi_2\varphi_3} - \dfrac{1}{\varphi_3\varphi_4}\right) - \left(\dfrac{\varphi_2 + \varphi_3}{\varphi_2^2\varphi_3^2} - \dfrac{\varphi_3 + \varphi_4}{\varphi_3^2\varphi_4^2}\right)\left(\dfrac{1}{\varphi_1\varphi_2} - \dfrac{1}{\varphi_2\varphi_3}\right)}$$

where t_1, t_2, t_3, and t_4 are observed temperatures corresponding to the fluidities φ_1, φ_2, φ_3, and φ_4, respectively.

Table I.—Water.

$\alpha = 0.24542$, $\beta = 296.15$, $\gamma = 3751.8$, $\delta = 94508$.

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
273.37	273.37	0.00	312.32	312.52	+0.06
274.13	273.99	—0.05	320.03	320.28	+0.07
276.09	275.53	—0.20	328.53	328.71	+0.05
277.47	276.82	—0.23	337.01	337.01	0.00
278.45	277.62	—0.29	345.54	345.60	+0.02
281.01	280.23	—0.27	353.75	353.72	—0.01
286.53	285.80	—0.25	362.90	362.77	—0.03
295.02	294.64	—0.13	371.09	371.02	—0.02
303.72	303.72	0.00	373.00	373.00	0.00
				Average,	0.09

Table II.—Octane.

$\alpha = 0.19074$, $\beta = 343.42$, $\gamma = 23{,}193$, $\delta = 1{,}325{,}100$.

Temp. observed.	Temp. calculated.	Percentage difference	Temp. observed.	Temp. calculated.	Percentage difference.
373.25	273.25	0.00	339.46	339.75	+0.08
285.18	284.52	—0.23	350.82	350.82	0.00
295.92	295.33	—0.19	361.33	361.52	+0.05
305.96	305.63	—0.10	371.52	371.30	—0.05
316.89	316.88	0.00	382.07	381.57	—0.13
327.73	328.12	+0.11	395.07	395.05	0.00
				Average,	0.08

Table III.—Isobutyric Acid.

$\alpha = 0.31190$, $\beta = 354.27$, $\gamma = 10{,}279$, $\delta = 276{,}425$.

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
276.69	276.69	0.00	361.06	361.07	+0.00
290.00	287.53	—0.08	371.94	372.37	+0.11
302.33	300.57	—0.58	382.78	383.05	+0.07
315.53	314.88	—0.20	395.97	393.65	—0.08
327.54	327.55	+0.00	407.50	407.16	—0.08
343.49	343.93	+0.12	420.47	420.51	+0.01
				Average,	0.11

Table IV.—Active Amyl Alcohol.

$\alpha = 0.26970$, $\beta = 335.66$, $\gamma = 1425.7$, $\delta = 7618.7$.

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
273.40	273.40	0.00	340.52	339.30	—0.06
284.63	279.36	—1.85	352.25	352.25	0.00
296.30	292.60	—1.24	364.88	363.31	—0.43
307.75	307.75	0.00	373.03	372.04	—0.26
320.40	322.13	+0.53	385.78	384.58	—0.31
329.94	329.62	—0.09	397.36	397.36	0.00
				Average,	0.38

The results of Tables I–IV show that van der Waal's equation may be used to reproduce fluidity data somewhat better than my simpler formula containing only three constants, but not nearly so well as my modified formula containing

four constants. Table V, giving the average percentage differences for the above compounds, will make this clearer.

Table V.—Average Percentage Differences from Using the Equations (1) $t = A\varphi - \frac{B}{\varphi} + C$, (2) $t = A\varphi - \frac{B}{\varphi + D} + C$, *and* (3) $T = \alpha\varphi - \beta - \frac{\gamma}{\varphi} + \frac{\delta}{\varphi^2}$.

Substance.	Average per cent. difference from (1).	Average per cent. difference from (2).	Average per cent. difference from (3).
Water	0.17	0.01	0.09
Octane	0.16	0.02	0.08
Isobutyric acid	0.43	0.06	0.11
Active amyl alcohol	1.17	0.08	0.38

On the one hand, we must recall that van der Waal's equation does not hold satisfactorily for volume, therefore the inferior agreement here exhibited does not prove that there is not an intimate relation between volume and fluidity. On the other hand, we recognize perfectly that such a relation would not be *proved* even if the same equation did hold accurately for both properties. My intention, at this time, is merely to call attention to the coincidence, and to try out formulas other than those already proposed.

The Abnormal Expansion Coefficient of Water at 4°.

With the purpose of testing further the possibility of a relationship between fluidity and volume, I made a study of the viscosity data of Thorpe and Rodger in the vicinity of 4°. They worked with special care and precision around this point with water, trying to detect abnormalities, but they were unable to detect any and properly point out that "the anomalous change in the density of water amounts to only 1 part in 10,000," hence one would hardly expect to find a maximum or minimum in so steep a curve as the fluidity curve. One would look only for a sagging or heaving in the curve. But as already noted, my modified equation holds for water with extreme accuracy, better, in fact, than for any other associated compound. Table VI gives the values

of the observed temperatures in the region of 4°, using the constants already calculated for water between 0° and 100°. Of the temperatures given in Table VI only one, marked with a (*), was used in deriving the constants:

Table VI.—Water.

$A = 0.23275$, $B = 8676.8$, $C = 309.17$, $D = 120.00$.

Temp. observed.	Temp. calculated.	Percentage difference.	Temp. observed.	Temp. calculated.	Percentage difference.
273.37*	273.37	0.00	277.47	277.46	—0.00
274.13	274.18	+0.02	278.19	278.19	0.00
274.86	274.87	+0.00	278.94	278.99	+0.02
275.41	275.43	+0.01	279.67	279.69	+0.01
276.09	276.03	—0.02	280.41	280.46	+0.02
276.84	276.81	—0.01	281.01	281.04	+0.01
				Average,	0.01

The correspondence between the calculated and observed values is truly remarkable, the more so when we examine carefully the calculated curves for other associated substances.[1] There we see that in reference to the first, middle, and last observations used in getting the constants, the calculated values of the temperature are usually first too small, then too large, and then again too small. In other words, my modified equation gives a curve which is probably invariably very slightly too sharply bent. The differences between the calculated and observed values, to be sure, are almost to the limit of experimental error, but *not quite*. If this is true, then water is exceptional among associated liquids in that at low temperatures the observed values of the temperature are smaller than would be expected. There is, therefore, in the case of water, a decrease in fluidity in the neighborhood of 4° to an amount of the same magnitude as the decrease in volume. It seems likely that this point could be definitely settled by applying my modified formula to a larger number of substances and proving that there is a constant deviation between the calculated and observed values as indicated.

[1] Z. physik. Chem., **66**, 252 and 253 (1909).

Critical Temperature.

It is a necessity of the human mind that the simplest relations appear first and that as the range of vision increases the complexity of phenomena becomes manifest. Thus, although we may grope for some simple relation between volume and fluidity at ordinary temperatures, we must recognize that over a broad range of temperature the relation cannot be entirely simple. Instead of fluidity continually increasing as the volume and temperature increase, the fluidity must pass through a maximum, since in gases the fluidity decreases with the temperature. There is no reason, however, for being disturbed over this fact since in liquids the viscosity is probably caused largely by the attraction between the particles, and in gases by the kinetic energy of the particles, and therefore we cannot expect a simple law to apply to both states of matter. It will be interesting to learn whether the maximum in fluidity is connected with the critical temperature. There seem to be no data on this point.

Vapor Pressure.

The fact that the fluidities of saturated aliphatic hydrocarbons and of ethers are for each class practically identical at the boiling points of the substances suggested the question as to whether this remarkable relation holds for other temperatures of equal vapor pressure. The data of Young and his collaborators enable us to give a partial answer to this question. The fluidity data are taken from the tables of Bingham and Miss Harrison,[1] as calculated from the viscosity data of Thorpe and Rodger. The fluidities and vapor pressures corresponding to every 10° of temperature, as given in Table VII, were plotted against each other and the result is seen in Figure I, where ordinates represent fluidities and abscissas vapor pressures in millimeters:

[1] Z. physik. Chem., **66**, 13 (1909).

Table VII.—Fluidities and Vapor Pressures of Aliphatic Hydrocarbons for Every 10°.

	Pentane.		Hexane.		Heptane.		Octane.	
Temp.	φ.	p. Young.	φ.	p. Thomas and Young.	φ.	p. Young.	φ.	p. Young.
0	353.4	183.25	252.3	45.45	192.4	11.45	142.1	2.94
10	391.2	281.8	281.8	75.00	217.5	20.50	163.4	5.62
20	430.8	420.2	312.4	120.0	243.6	35.50	185.9	10.45
30	472.1	610.9	344.8	185.4	271.2	58.35	209.1	18.40
40	(513.6)	873.0	378.8	276.7	299.5	92.05	233.6	30.85
50			414.9	400.9	329.9	140.9	259.4	49.35
60			452.7	566.2	362.1	208.9	286.4	77.55
70			(494.6)	787.0	395.0	302.3	314.5	117.9
80					431.0	426.6	344.3	174.8
90					468.3	588.8	376.2	253.5
100					(511.2)	795.2	409.0	353.6
110							443.5	481.9
120							482.0	646.4
130							(523.0)	859.0

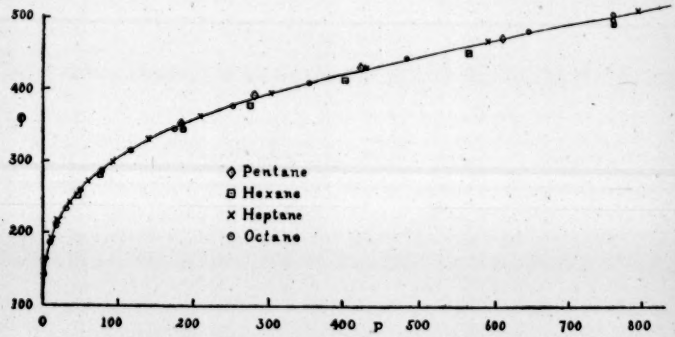


Figure I.—fluidity-vapor pressure curve of the aliphatic hydrocarbons.

It is seen that the fluidity-vapor pressure curves of the available aliphatic hydrocarbons lie closely together. This extraordinary result proves that fluidity and vapor pressure are closely related, presumably due to the fact that both are

dependent upon the intermolecular forces. Since the fluidity-vapor pressure curve becomes continually more and more nearly linear it is worth while to point out that probably for very high fluidities the vapor pressure is directly proportional to the fluidity.

EXPERIMENTAL.

Having reached the above results with the data at hand, it became highly desirable to measure the vapor pressures of the ethers whose fluidities were known in order to see in how far they behave like the hydrocarbons. This work was done at the University of Chicago during the summer of 1909, and I am highly indebted for the courtesy shown me there and for the use of apparatus from both the Kent Chemical Laboratory and the Ryerson Physical Laboratory.

In measuring vapor pressure, the dynamical method of Ramsay and Young[1] was used. However, as ethers were to be used, rubber connections were avoided wherever the ether would come into contact with them. A small dropping funnel with glass stopcock and stopper was used. The joints were ground with the finest emery until they were close-fitting, and stopcock grease could be avoided. A trace of phosphoric acid was occasionally used as a lubricant, but generally the ethers themselves served for this purpose, and to keep air from leaking in. The tube of the dropping funnel was properly bent and drawn out to deliver the ether on cotton wound on the stem of a thermometer. The cotton was extracted with ether, dried and kept in a desiccator until used. The thermometers were of the Gerhardt type, nitrogen-filled. They were tested by immersion in ice and in a boiling-point apparatus for testing thermometers, and the corrections were applied to all observations. One thermometer extended from —5° to 55° and the other from 45° to 105°. The ends of the dropping funnel and the thermometer were forced through two holes in a good cork and the whole tightly fitted into a large test tube, to which had been sealed a side tube leading to a receiver. The test tube was heated by means of a bath

[1] J. Chem. Soc., **47**, 42 (1885).

consisting of a large beaker of water, which was stirred. The receiver was cooled with a mixture of ice and salt. From the receiver a tube led to the manometer, made especially for this purpose by Boehm & Co. It consisted of an ω-tube, one end of which was closed, filled with freshly-distilled mercury, and boiled out. The manometer, however, was not entirely satisfactory, as even after a second boiling out there remained a microscopic air bubble at the top of the tube. This appeared to increase somewhat during the course of the investigation. Repeated tests were made as to the possible effect of this source of error. Corrections were made for it where necessary. Finally the manometer was connected to a large bottle which served as a reservoir and this, in turn, was connected to an aspirator. A thermometer, hung beside the manometer, was of use in correcting the mercurial heights. The two arms of the manometer, which contained mercury, were of large and nearly equal bore, so that no correction for capillarity was necessary. The heights were read by means of a cathetometer about six feet distant, and sighted simultaneously on the manometer and on a steel tape suspended freely directly between the two limbs of the manometer. The tape naturally hung straight, but a small bob on the end also tended to ensure this. A Lufkin tape was selected which appeared to have very slight variations from the mean. It was then compared throughout its length with a standard meter at the temperature of the room, and a curve of corrections was constructed. Corrections for the expansion and contraction of the tape as the investigation proceeded were negligible, as were also corrections for the difference of level of the experimental tube and manometer, and for the latitude and altitude of Chicago.

It was necessary that the cross hairs of the cathetometer telescope should remain horizontal. This was ensured by giving the instrument a firm and level base and adjusting the wires by sighting at the edge of a level. This was tested repeatedly during the investigation.

The ethers investigated were methylpropyl, ethylpropyl, and dipropyl ether. As a control experiment, diethyl ether

was also purified and tested and values were obtained which were in harmony with those found by Ramsay and Young. The ethers were prepared according to the methods used by Thorpe and Rodger[1] in making the same ethers for viscosity determinations. They were dried for weeks over sodium wire and fractionally distilled with a Glinsky distilling head. Finally the observations were repeated for each of the substances, with different samples of the liquids, over part of the curve to confirm the results.

The corrected values of the vapor pressures are given in Tables VIII, IX, and X:

Table VIII.—Vapor Pressure of Methylpropyl Ether.

Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.
−0.60	15.18	21.01	38.83	31.87	59.40
3.42	18.00	23.00	42.05	32.72	61.25
7.01	21.26	23.91	43.60	33.80	63.39
8.81	23.09	24.85	45.33	34.84	65.81
12.58	27.22	26.80	48.75	35.58	67.52
14.30	29.33	28.25	51.76	36.73	70.38
18.67	35.26	29.06	53.34	38.34	73.95
17.60	33.69	30.12	55.59	39.34	76.56
20.02	37.60	31.01	57.45		

Table IX.—Vapor Pressure of Ethylpropyl Ether.

Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.
−1.02	4.98	26.40	18.80	56.23	59.06
−0.30	5.18	28.85	20.87	57.44	61.62
5.01	6.90	31.15	23.19	57.99	62.65
6.62	7.46	33.92	25.85	58.68	64.31
6.68	7.48	38.10	30.52	59.50	65.88
9.00	8.44	39.98	32.78	60.86	69.00
11.26	9.41	42.68	36.30	61.19	69.84
13.92	10.65	45.03	39.73	61.72	70.74
16.51	12.07	47.97	44.23	62.66	73.17
17.72	12.78	49.36	46.60	63.20	74.43
20.72	14.78	52.41	52.00	63.40	74.92
23.30	16.58	54.00	54.78	63.78	75.64
26.25	18.76	55.79	58.31		

[1] Phil. Trans., **189**, A, 103 (1897).

Table X.—Vapor Pressure of Dipropyl Ether.

Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.	Temp. C°.	Press. in cm.
8.80	2.99	45.23	15.50	77.40	51.76
11.95	3.42	49.53	18.49	79.00	54.69
18.40	4.73	57.50	25.51	80.40	57.21
21.42	5.54	59.70	27.84	81.80	59.80
24.05	6.21	62.47	30.98	83.19	62.50
27.61	7.37	66.30	35.62	84.75	65.46
28.71	7.69	70.01	40.41	86.10	68.24
33.01	9.54	71.99	43.26	86.89	70.14
41.60	13.41	73.60	45.66	88.78	74.11

These values were plotted on a large scale and the vapor pressures for every 10° read off from the curves. These values are given in Table XI, together with the corresponding fluidities. These last values were plotted against each other, as was done with the hydrocarbons, and the result is shown in Fig. II.

Table XI.—The Corresponding Vapor Pressures and Fluidities of Ethers for Every 10° Centigrade.

	Methylpropyl ether.		Ethylpropyl ether.		Dipropyl ether.		Diethyl ether.	
Temp.	p in mm.	φ.	p in mm.	φ.	p in mm.	φ.	p in mm. Ramsay and Young.	φ.
0°	156.0	325.5	52.1	252.1	22.4	185.2	184.9	350.9
10°	242.6	361.0	88.5	282.5	31.8	210.3	291.78	387.2
20°	373.4	397.3	142.6	314.9	51.0	238.1	442.36	426.5
30°	552.5	437.0	219.5	349.0	82.0	266.7	647.92	467.3
40°	784.0	476.7	327.9	384.7	125.6	296.4	921.18	511.4
50°			476.7	422.1	189.6	328.2		
60°			670.2	462.5	281.8	360.9		
70°					404.2	395.9		
80°					563.6	432.6		
90°					776.0	472.5		

Fig. II shows that the fluidity-vapor pressure curves for ethers fall together into a single curve about as well as they do for the hydrocarbons, and the character of the curve is entirely similar, indicating again that *at high temperatures the fluidity is a linear function of the vapor pressure.* It is interesting to observe the possibility of predicting either the fluidity or the vapor pressure of any compound of these classes

of which either the vapor pressure or the fluidity, respectively, is known, or can be calculated. In fact, fluidities of compounds of these classes can be calculated, since they are unassociated. A word will be added on this point later in this paper.

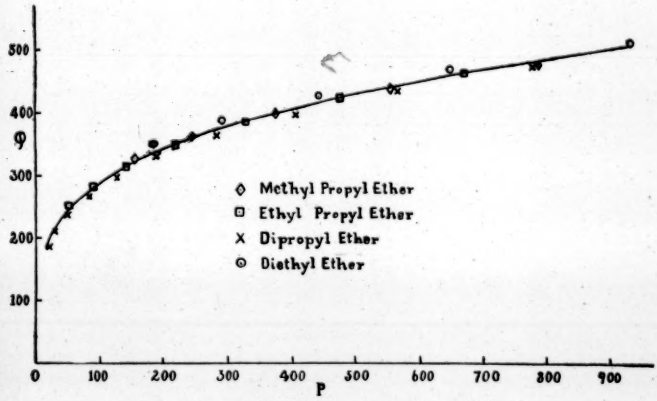


Figure II.—Fluidity-vapor pressure curve of the ethers.

Corresponding Condition.

Putting in other words the results of the examination of the fluidity-vapor pressure curves, I may state that *at temperatures corresponding to any given vapor pressure all aliphatic hydrocarbons and all ethers have nearly identical fluidities*, or, conversely, *at temperatures corresponding to any given fluidity the vapor pressures of these compounds are equal.* It was long ago observed that at temperatures of equal vapor pressure, particularly at the ordinary boiling point, substances are in a "corresponding condition." It is evident, therefore, at least for aliphatic hydrocarbons and ethers, that *when the liquids of a given class have equal fluidities, they are in a "corresponding condition."* It will be worth while to make a further investigation along this line with other classes of

unassociated compounds, as iodides and bromides. It is certain that associated compounds will give fluidity-vapor pressure curves which neither fall together in a single curve nor have any apparently simple relation to each other. To understand this would probably necessitate a knowledge of the cause of association and the laws governing it.

Temperature Coefficient of Association.

In a previous paper,[1] in calculating association, only the fluidity 200 was used for comparison, therefore it seemed desirable to make a comparison at some other fluidity in order to see how well different results agree by this method and also in order to obtain a temperature coefficient of association. For this purpose the fluidity 300 was selected. The following tables show how the constants were obtained:

Table XII.—Value of a Methylene Grouping at the Fluidity 300.

Substance.	Absolute temperature observed.	Difference.
Pentane	(258.2)	
		30.5
Hexane	288.7	
		24.4
Heptane	313.1	
		24.7
Octane	337.8	
Isopentane	(253.8)	
		29.2
Isohexane	283.0	
		22.3
Isoheptane	(305.3)	
Isoprene	(250.0)	
		24.4
Diallyl	274.4	
Methyl iodide	(338.5)	
		20.8
Ethyl iodide	(359.3)	
		23.2
Propyl iodide	(382.5)	
Isopropyl iodide	(371.6)	
		23.5
Isobutyl iodide	(595.1)	
Ethyl bromide	(311.5)	
		29.0
Propyl bromide	340.5	
Isopropyl bromide	(331.0)	
		26.8
Isobutyl bromide	357.8	
Isopropyl chloride	289.8	
		32.7
Isobutyl chloride	322.5	
Methylpropyl ether	265.5	
		22.9
Ethylpropyl ether	288.4	
		25.8
Dipropyl ether	314.2	
Methylisobutyl ether	284.9	
		19.6
Ethylisobutyl ether	304.5	

[1] Z. physik. Chem., 66, 26 (1909).

If the mean of the above differences, 25.4, is taken as the value of a methylene grouping, it becomes possible to calculate the value of the hydrogen atom. First, however, it is important to find the value of the *iso* grouping:

Table XIII.—Value of the Iso Grouping at Fluidity 300.

Substance.	Normal position.	Iso position.	Difference.
Pentane	258.2	253.8	4.4
Hexane	288.7	283.0	5.7
Heptane	313.1	305.3	7.8
Propyl iodide	382.5	371.6	10.9
Propyl bromide	340.5	331.0	9.5
Propyl chloride	298.7	289.8	8.9
Butyric acid	426.5	416.7	9.8
Methyl butyrate	343.2	334.2	9.0

The value of the iso compound is on the average 8°.2 lower than that of the normal compound.

Table XIV.—Value of Hydrogen at Fluidity 300.

Substance.	Temperature observed.	Temperature calculated. $n \times CH_2$.	Difference.
Pentane	258.2	127.0	131.2
Hexane	288.7	152.4	136.3
Heptane	313.1	177.8	135.3
Octane	337.8	203.2	134.6
Isohexane	283.0	144.2	138.8
Isoheptane	305.3	169.6	135.7

This gives 135.6 as the value for H_2, 67.8 for H, and —110.2 for C.

The value of the double bond is obtained from the following table:

Table XV.—Value of the Double Bond at Fluidity 300.

Substance.	Normal.	Allyl.	Difference.
Iodide	382.5	380.5	2.0
Bromide	340.5	336.5	4.0
Chloride	298.7	291.9	6.8

It is seen that for a fluidity of 300, the value for an allyl compound is about 4°.3 lower than for the normal compound,

which contains 2 atoms of hydrogen more. Therefore a double bond is equivalent to 131.3.

The value for oxygen is determined by means of the ethers:

Table XVI.—The Value of Oxygen at Fluidity 300.

Substance.	Temperature observed.	Temperature calculated. C_nH_{2n+2}.	Difference.
Methylpropyl ether	265.5	237.2	28.3
Ethylpropyl ether	288.4	262.6	25.8
Dipropyl ether	314.2	288.0	26.2
Methylisobutyl ether	284.9	254.4	30.5
Ethylisobutyl ether	304.5	279.8	24.7
		Average,	27.1

For the determination of association in aromatic compounds it is necessary to get the value of the ring grouping, if, as in our preceding paper, we assume the benzene formula of Kekulé with 3 double bonds. This is done in Table XVII.

Table XVII.—Value of the Benzene Ring at Fluidity 300.

Substance.	Temperature observed.	Temperature calculated. C_nH_{2n-6}.	Difference.
Benzene	348.1	139.5	208.6
Toluene	347.5	164.9	182.6
Ethylbenzene	362.1	190.3	171.8
o-Xylene	377.5	190.3	176.2
m-Xylene	355.5	190.3	164.2
p-Xylene	357.4	190.3	167.1

The differences vary widely from each other. If, as before, it is assumed that this is due to unlike association in these hydrocarbons, then we may take the smallest value, *viz.*, 164.2, as the maximum value of the constant. Since *m*-xylene may be somewhat associated, it is evident that associations calculated with this constant are minimum values. Hence, where this constant is used the association will be marked with a + sign.

In Table XVIII I have grouped together for comparison the constants at fluidities 200 and 300:

Table XVIII.—Constants at Fluidity 200 and Fluidity 300.

Atom or grouping.	$\varphi = 200$.	$\varphi = 300$.	Atom or grouping.	$\varphi = 200$.	$\varphi = 300$.
Carbon	—95.7	—110.2	Iso	—7.6	—8.2
Hydrogen	59.2	67.8	Double bond	114.4	131.3
Oxygen	24.2	27.1	Benzene ring	141.8	164.2

Using these constants, the temperatures corresponding to a fluidity of 300 were calculated for a large number of associated compounds. The observed temperatures are invariably higher than the temperatures calculated from the constants derived from unassociated compounds. Since the values of the constants are additive, it is evident that the association is obtained by simply dividing the observed by the calculated values. From the associations at fluidities 200 and 300 and the temperatures corresponding to these fluidities the temperature coefficient of association, *i. e.*, the mean decrease in the association (between the temperature limits indicated) for a rise in temperature of 1° C., is calculated. These results are given in Table XIX. Column 2 gives the observed temperatures corresponding to a fluidity of 300, column 3 the calculated temperature, and column 4 the association for that fluidity. Column 5 gives the association already calculated for a fluidity of 200 and column 6 the temperature coefficient of association.

The results are perhaps most noteworthy in the close agreement between the association at the two fluidities. Usually the decrease in association as the temperature is raised is very small, but it is considerable in water and the alcohols, and this is true in spite of the fact that some other substances are even more highly associated. Thus, acetic acid is highly associated, but the temperature coefficient of association is much smaller than that for amyl alcohol, which is very much less associated over the range of temperature studied. Evidently amyl alcohol is very highly associated at low temperatures. All of these facts are in harmony with conclusions already drawn from a study of the fluidity curves over a large temperature range.[1]

[1] Z. physik. Chem., **66**, 7 *et seq.* (1909).

Table XIX.—Temperature Coefficients of Association.

Substance.	Temperature observed. $\varphi = 300$.	Temperature calculated. $\varphi = 300$.	Association. $\varphi = 300$.	Association. $\varphi = 200$.	Temperature coefficient.
Water	358.5	162.7	2.20	2.31	0.0038
Dimethyl ketone	289.5	207.5	1.23	1.23	0.000
Diethyl ketone	326.5	285.4	1.14	1.14	0.000
Methylethyl ketone	315.6	260.0	1.21	1.22	0.000
Methylpropyl ketone	330.0	285.4	1.17	1.16	0.000
Acetic acid	407.9	236.3	1.73	1.77	0.001
Propionic acid	408.5	261.7	1.55	1.57	0.001
Butyric acid	426.5	287.1	1.48	1.51	0.001
Isobutyric acid	416.7	278.9	1.49	1.51	0.001
Acetic anhydride	388.1	309.9	1.25	1.25	0.000
Propionic anhydride	402.4	360.7	1.11	1.12	0.000
Benzene	348.1	303.7	1.14+	1.17+	0.001
Toluene	347.5	329.1	1.06+	1.06+	0.000
Ethylbenzene	362.1	354.5	1.02+	1.02+	0.000
o-Xylene	377.5	354.5	1.06+	1.07+	0.000
m-Xylene	355.5	354.5	1.00+	1.00+	0.000
p-Xylene	357.4	354.5	1.00+	1.00+	0.000
Methyl alcohol	336.9	188.1	1.79	1.84	0.002
Ethyl alcohol	(371.5)	213.5	(1.74)	1.83	0.003
Active amyl alcohol	(408.7)	289.7	(1.41)	1.54	0.005
Inactive amyl alcohol	(415.5)	289.7	(1.30)	1.55	0.008
Allyl alcohol	378.7	234.6	1.61	1.69	0.003
Methyl formate	297.5	236.3	1.26	(1.25)	0.000
Ethyl formate	311.4	261.7	1.19	1.19	0.000
Propyl formate	333.9	287.1	1.16	1.17	0.000
Methyl acetate	306.0	261.7	1.17	(1.17)	0.000
Ethyl acetate	320.8	287.1	1.12	1.12	0.000
Propyl acetate	343.0	312.5	1.09	1.11	0.001

It may be noted here that it is possible to calculate the general fluidity equation of an unknown substance. The slopes of the fluidity curves of a number of classes of compounds for a fluidity of 200[1] and the constants for fluidities 200 and 300 have been given. Since the slope in a given class remains constant and the absolute temperature corresponding to fluidities of 200 and 300 can be calculated, the constants in the equation $t = A\varphi - \frac{B}{\varphi} + C$ may be found.

[1] Z. physik. Chem., **66**, 27 *et seq.* (1909).

Having found the fluidity curve, it becomes theoretically possible to calculate the vapor pressure curve, as already pointed out.

The Kekulé Formula for Benzene.

I have shown that oxygen has the same value in all compounds, whereas viscosity workers have heretofore found it necessary to give oxygen different values in the different classes of compounds. I have regarded this as a strong evidence in favor of the correctness of my hypothesis that fluidities, and not viscosities, are additive. But it was necessary to assume a value for a benzene grouping, as did also Thorpe and Rodger, when I started out on the hypothesis that benzene contained 3 double bonds according to the Kekulé formula. But there is another way of regarding the matter. For C_6H_6 differs from the corresponding aliphatic hydrocarbon C_6H_{14} by 8 hydrogen atoms. Now we have seen that 2 hydrogen atoms equal 135.6 at a fluidity of 300. And without any hypothesis as to what a "double bond" may be, we have the fact that an allyl compound contains 2 hydrogen atoms less than the corresponding saturated compound, yet the temperature is only 4°.3 lower than for the saturated compound at the same fluidity of 300. Hence we may say that the compound compensates in some way for the loss of the 2 hydrogen atoms to the extent of 131.3, but since benzene has 8 less hydrogen atoms than the saturated compound, the simplest assumption is that the loss will be compensated for to the extent of $4 \times 131.3 = 525.2$. Recalculating the association of the aromatic hydrocarbon on this assumption, we obtain the following table:

Table XX.—Association of Aromatic Hydrocarbons at Fluidity 300 without Assuming the Kekulé Formula for Benzene with Three Double Bonds.

Substance.	Temperature observed.	Temperature calculated. C_nH_{2n-6}.	Association.
Benzene	348.1	270.8	1.29
Toluene	347.5	296.2	1.17
Ethylbenzene	362.1	321.6	1.13
o-Xylene	377.5	321.6	1.17
m-Xylene	355.5	321.6	1.11
p-Xylene	357.4	321.6	1.11

The values calculated earlier were admittedly minimum values. These values therefore have a certain advantage. It is impossible to affirm at this stage of the work that the ring grouping does not have a value, hence these may be maximum values. These values are in fact somewhat higher than the values for these substances determined by other workers.

Association in Mixtures.

Having found it possible to calculate the association of pure liquids with success by making use of the fluidity data, it seemed advisable to investigate liquid mixtures with the hope of learning something as to their condition in regard to chemical combination or association. In getting the association of liquids a certain fluidity was chosen and the temperatures calculated at which each liquid should have this fluidity. Unfortunately, the viscosities of liquid mixtures have been measured at only a few temperatures at the most, hence the comparison at a given fluidity cannot be made without much new experimental work on these mixtures. I have tried to work out a method of comparison at a given temperature, but while some interesting relations were brought out, assumptions seemed necessary which destroy the usefulness of the method. Of course there is also a theoretical objection to making a comparison at constant temperature, since the substances would be very far from being in a "corsponding condition" as is the case when the temperatures of equal fluidities are compared. My next work will therefore be to measure the viscosities of a series of mixtures over a range of temperature.

CONCLUSIONS.

1. A summary has been given of the evidence accumulated thus far to prove that fluidities and not viscosities are additive.

2. Attention was called to the identity of the equation proposed in 1906 with the equation derived in 1909, tested and proved satisfactory for a large number of substances.

3. The possibility of a connection between volume and

fluidity was noted. Van der Waal's equation in terms of volume, when the pressure is constant, is very similar to my simple equation. Moreover, on substituting fluidity in place of volume this equation reproduces fluidity (or viscosity) data with greater fidelity than any equation heretofore proposed except my modified equation.

4. A careful examination of the fluidity curve of water in the region of 4° indicates a sagging of the curve coincident with the minimum in volume.

5. Since the fluidity of liquids increases with the temperature, and the fluidity of gases decreases with the temperature, there must be a maximum in fluidity and it is proposed to investigate whether or not this lies at the critical point.

6. Since it was observed that the fluidities of all aliphatic hydrocarbons and all ethers are nearly identical at their boiling points, it seemed desirable to learn whether or not this relation between fluidity and vapor pressure was general. The data at hand have proved it to be so for the hydrocarbons.

7. Measurements of the vapor pressures of methylpropyl ether, ethylpropyl ether, and dipropyl ether were made between 0° C. and their boiling points. The relation between fluidity and vapor pressure at their boiling points was also found to be general in the case of the ethers.

8. Furthermore, it appears to be true that at high temperatures the fluidity is a linear function of the vapor pressure.

9. Evidence has been given to prove that at temperatures of equal fluidity substances are in corresponding condition.

10. The "constants" corresponding to a fluidity of 300 have been given and the association of a number of substances calculated. From these values and those obtained previously the temperature coefficients of association have been calculated. In spite of using different substances for calculating the constants, the values of the association at the different fluidities are entirely harmonious.

11. Future work on liquid mixtures has been outlined.

RICHMOND COLLEGE,
RICHMOND, VA.,
JAN. 12, 1910.

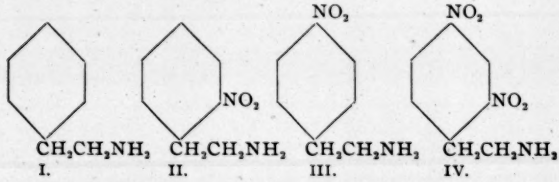
[Contributions from the Sheffield Laboratory of Yale University.]

CLXXVIII.—RESEARCHES ON AMINES: SYNTHESES OF 4-NITROPHENYLETHYLAMINE AND 2,4-DINITROPHENYLETHYLAMINE.

[SECOND PAPER.]

By Treat B. Johnson and Herbert H. Guest.

The three possible mononitrobenzylamines[1] (*o*,- *m*- and *p*-) have been synthesized, but no nitro derivatives of the simplest β-amine of the aromatic series, phenylethylamine, I, are described in Beilstein's *Handbuch*. It was therefore of interest, in our study of β-amines and their substitution products, to investigate the nitro derivatives of this base. We describe in this paper, the preparation and properties of *p*-nitrophenylethylamine, III, 2,4-dinitrophenylethylamine, IV, and incidentally several derivatives of these two bases and also of *o*-nitrophenylethylamine, II.



I. II. III. IV.

It is a well-known fact that, in the nitration of acetanilide, the acetyl group favors substitution in the *para* position. This amide reacts with nitric acid, giving an excellent yield of *p*-nitroacetanilide[2] (95 per cent. of the theoretical), while benzanilide gives a mixture of the three mononitro derivatives (*o*-, *m*- and *p*-), in which the *ortho* and *para* compounds are present in about equal proportions.[3] Acetylbenzylamine[4] also reacts with nitric acid, giving chiefly acetyl-*p*-nitro-

[1] Gabriel: Ber. d. chem. Ges., **20**, 2228. Gabriel and Hendess: *Ibid.*, **20**, 2869. Gabriel and Jansen: *Ibid.*, **24**, 3092. Hafner: *Ibid.*, **23**, 338.

[2] Nölting and Collins: *Ibid.*, **17**, 262.

[3] Hübner: Ann. Chem. (Liebig), **208**, 292.

[4] Strakosch: Ber. d. chem. Ges., **5**, 697. Rudolph: *Ibid.*, **12**, 1297.

benzylamine.[1] These observations suggested that the introduction of a nitro group into the *para* position in phenylethylamine would be effected smoothly by nitration of acetylphenylethylamine.[2] The results of our experiments confirmed this assumption.

Acetylphenylethylamine, VII, was prepared for our work by acetylation of phenylethylamine with thioacetic acid. We now find that this amide reacts smoothly with nitric acid (sp. gr. 1.51) below 5°, giving a mixture of the *ortho-* and *paranitro* acetyl derivatives, X and XI. The *para* compound, however, is the chief product of the reaction, under these conditions, and the yield corresponds to about 70 per cent. of the theoretical. The formation of a dinitro derivative was not observed. Acetyl-2,4-dinitrophenylethylamine, VIII, however, is obtained when acetylphenylethylamine is nitrated in the presence of concentrated sulphuric acid. The structures of this dinitro compound, VIII, and of acetyl-*p*-nitrophenylethylamine, XI, were established by the facts that they were converted into 2,4-dinitrobenzoic[3] and *p*-nitrobenzoic[4] acids, respectively, by oxidation with potassium dichromate and sulphuric acid. The nitrophenylethylamines, XIII, XII, and IX, are formed quantitatively by hydrolysis of their corresponding acetyl derivatives with hydrochloric and hydrobromic acids.

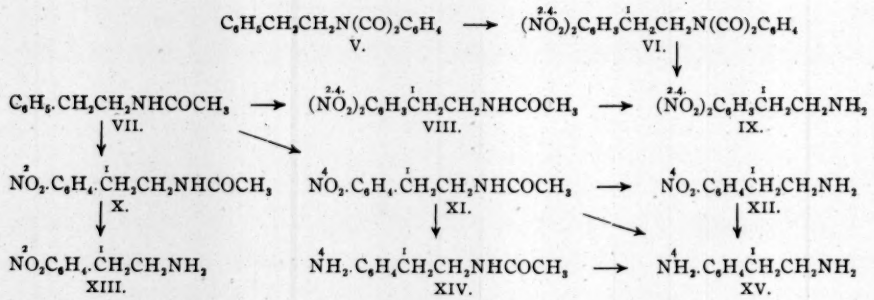
Especially interesting was the action of nitric acid (sp. gr. 1.51) on phthalylphenylethylamine, V, under the same conditions as are favorable for the formation of a mononitro derivative from acetylphenylethylamine. The chief product of the reaction, in this case, was phthalyl-2,4-dinitrophenylethylamine, VI, and it was with some difficulty that we were able to isolate a mononitro derivative sufficiently pure for analysis. The structure of this dinitro compound, VI, was determined by the fact that it gave, on hydrolysis, the same

[1] Amsel and Hofmann: Ber. d. chem. Ges., **19,** 1286.

[2] Bischler and Napieralski: Ber. d. chem. Ges., **26,** 1905. Michaelis and Simon: *Ibid.*, **26,** 2167.

[3] Tiemann and Judson: Ber. d. chem. Ges., **3,** 223. Griess: *Ibid.*, **7,** 1225. Hübner: Ann. Chem. (Liebig), **222,** 79.

[4] Beilstein and Wilbrand: Ann. Chem. (Liebig), **128,** 257. Beilstein and Geitner: *Ibid.*, **139,** 335.


C6H5CH2CH2N(CO)2C6H4
V.
(2.4.NO2)2C6H3 1CH2CH2N(CO)2C6H4
VI.
C6H5.CH2CH2NHCOCH3
VII.
(2.4.NO2)2C6H3 1CH2CH2NHCOCH3
VIII.
(2.4.NO2)2C6H3 1CH2CH2NH2
IX.
2NO2.C6H4.1CH2CH2NHCOCH3
X.
4NO2.C6H4.1CH2CH2NHCOCH3
XI.
4NO2.C6H4 1CH2CH2NH2
XII.
2NO2C6H4.1CH2CH2NH2
XIII.
4NH2.C6H4 1CH2CH2NHCOCH3
XIV.
4NH2.C6H4 1CH2CH2NH2
XV.

dinitrophenylethylamine, IX, as was obtained by hydrolysis of acetyl-2,4-dinitrophenylethylamine, VIII.

The acetyl derivatives of *ortho-* and *para*nitrophenylethylamines and also of 2,4-dinitrophenylethylamine are weak bases, whose salts undergo dissociation in water. Acetyl-*o*-nitrophenylethylamine, X, is apparently more basic than the isomeric *para* compound, XI. Acetyl-*p*-nitrophenylethylamine is converted quantitatively into acetyl-*p*-aminophenylethylamine, XIV, by reduction with aluminium amalgam. This is a strong diacid base and forms a stable dihydrochloride. On the other hand, when reduced with tin and hydrochloric acid the amide underwent hydrolysis, with loss of the acetyl group, giving *p*-aminophenylethylamine, XV. This behavior is perfectly analogous to that of acetyl-*p*-nitrobenzylamine, under the same conditions, which is converted smoothly into *p*-aminobenzylamine.[1]

An attempt to synthesize *p*-aminophenylethylamine, XV, by reduction of *p*-aminobenzyl cyanide[2] with sodium and alcohol was unsuccessful. This nitrile, to our surprise, was reduced abnormally, giving an excellent yield of *p*-toluidine. Other alkyl nitriles, it has been observed, are reduced in this abnormal manner. Toluene is invariably formed, as a by-product, in the reduction of benzyl cyanide with sodium and alcohol. Bamberger and Immerwahr[3] observed that diphenylacetonitrile is reduced, under these conditions, giving a mixture of diphenylmethane and *unsymmetrical* diphenylethylamine. It is of interest to note also, in this connection, that one reason for a small yield of *p*-hydroxyphenylethylamine, by reduction of *p*-hydroxybenzyl cyanide with sodium and alcohol,[4] is that part of the nitrile is reduced abnormally, giving *p*-cresol.

After the completion of the work described in this paper a publication by Barger and Walpole[5] appeared, in which they describe the action of fuming nitric acid on benzoylphenyl-

[1] Ber. d. chem. Ges., **19**, 1286.
[2] Pschorr, Wolfes and Buchow: *Ibid.*, **33**, 162.
[3] *Ibid.*, **33**, 2845.
[4] Barger: J. Chem. Soc., **95**, 1123 (1909).
[5] *Ibid.*, **95**, 1720.

ethylamine and acetylphenylethylamine. They observed that substitution took place in the *para* positions and obtained a yield of benzoyl-*p*-nitrophenylethylamine corresponding to only 35 per cent. of the calculated amount. The results obtained by nitration of the acetylphenylethylamine were less satisfactory and the yield of *p*-nitro compound is not given. The corresponding *ortho* derivatives were not isolated.

EXPERIMENTAL PART.

Acetylphenylethylamine, $C_6H_5CH_2CH_2NHCOCH_3$.—We prepared this amide[1] by acetylation of phenylethylamine with thioacetic acid. Fifty-three grams of the freshly distilled amine were placed in a dry flask, connected with a reflux condenser, and 40 grams of thioacetic acid (1 mol. = 33.3 grams) then added slowly to the amine through the condenser tube. There was an immediate reaction with evolution of heat and formation of hydrogen sulphide. After addition of the thio acid the mixture was heated in an oil bath at 210°–220° for 1 hour and finally for a few minutes, at 290°, in a sand bath to remove the excess of thioacetic acid. On cooling, the amide completely solidified and was used for our experiments without further purification. The yield was 70 grams, or 98 per cent. of the theoretical.

Acetyl-p-*nitrophenylethylamine*, $(p)NO_2C_6H_4CH_2CH_2NHCOCH_3$.—An excellent yield of this amide is easily obtained by nitration of acetylphenylethylamine under the following conditions: Thirty-five cc. of nitric acid (sp. gr. 1.51) are cooled to 0° and 10 grams of the amide added slowly. The amide dissolves immediately with evolution of heat and in order to obtain the best results it is advisable not to allow the temperature of the solution to rise above 5°. After allowing to stand for 10–15 minutes the acid solution is diluted with ice water until it assumes a turbid appearance and the nitric acid then neutralized, at a low temperature, with ammonia. The amide separates in prismatic crystals which usually melt at 130°–140°. After nitration of 70 grams of acetylphenylethylamine, under these

[1] Bischler and Napieralski: *Loc. cit.* Michaelis and Simon: *Loc. cit.*

conditions, 55 grams of the *p*-nitro compound, corresponding to about 62 per cent. of the theoretical yield, separated after neutralization with ammonia. The amide is very soluble in hot and moderately soluble in cold alcohol. It is soluble in boiling water, but separates on cooling as an oil, which soon crystallizes in colorless, prismatic crystals melting at 141°–142° if heated rapidly. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{12}O_3N_2$.	Found. I.	II.
N	13.46	13.5	13.7

In order to isolate the other products of this reaction the ammoniacal filtrate, after filtering off the acetyl-*p*-nitrophenylethylamine, was concentrated on the steam bath, until ammonium nitrate began to separate, and cooled. We obtained about 15 grams of crystalline material which proved to be a mixture of acetyl-*p*-nitrophenylethylamine and the isomeric *ortho* derivative melting from 90°–120°. They were easily separated by trituration with cold dilute hydrochloric acid, in which the *ortho* compound is very soluble (see below). The insoluble *para* compound was then dried on a porous plate and recrystallized once from 95 per cent. alcohol. We recovered in this manner 3.5 grams melting at 135°–137.°

Acetyl-o-nitrophenylethylamine, $(o)NO_2C_6H_4CH_2CH_2NHCOCH_3$.—When the hydrochloric acid solution above was neutralized with ammonia this compound separated as an oil which solidified when cooled at 0°. It was then dried on a porous plate to free it from oil and purified by repeated crystallizations from dilute alcohol and benzene. It was easily soluble in boiling benzene but separated on cooling in slender prisms melting at 86°–88° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{12}O_3N_2$.	Found.
N	13.4	13.11

This amide undergoes hydrolysis when digested with hydrobromic acid, giving the hydrobromide of o-*nitrophenylethyl-*

amine. The free base separated as an oil, heavier than water, when the salt was decomposed by alkali, and gave a crystalline picrate, which was soluble in alcohol and melted at 147° to an oil.

*Oxidation of Acetyl-*p*-nitrophenylethylamine with Potassium Dichromate.*—Seventh-tenths gram of the nitro compound was oxidized for 1.5 hours at 100° with 2.5 grams of potassium dichromate, dissolved in a mixture of 5 cc. of concentrated sulphuric acid and 15 cc. of water. The solution assumed a green color and prismatic crystals slowly deposited from the hot solution. After cooling, they were separated by filtration and purified by crystallization from hot water. The substance melted at 237°–238° and was identified as *p*-nitrobenzoic acid.[1] A mixture of this oxidation product and the pure *p*-nitro acid melted at the same temperature. Analysis (Kjeldahl):

	Calculated for $C_7H_5O_4N$.	Found.
N	8.38	8.37

*Hydrochloride of Acetyl-*p*-nitrophenylethylamine,* $(p)NO_2C_6H_4CH_2CH_2NHCOCH_3.HCl$.—The amide is a weak base and dissolves in concentrated hydrochloric acid, giving a stable salt which can be digested with hydrochloric acid for hours without change. One gram was dissolved in 20 cc. of boiling acid and the solution cooled, when the hydrochloride separated in prisms, melting at 179°–180°, with effervescence, to a dark oil. It is very soluble in cold, absolute alcohol and dissociates in water, giving the free amide melting at 141°–142°. Analysis:

0.1064 gram substance gave 0.0613 gram AgCl.

	Calculated for $C_{10}H_{13}O_2N_2.HCl$.	Found.
Cl	14.51	14.24

p - *Aminophenylethylamine,* $(p)NH_2C_6H_4CH_2CH_2NH_2$. — A quantitative yield of the hydrochloride of this base can be obtained by reduction of acetyl-*p*-nitrophenylethylamine with tin and hydrochloric acid. One gram of the amide was dis-

[1] *Loc. cit.*

solved in a mixture of 10 cc. of 95 per cent. alcohol and 10 cc. of concentrated hydrochloric acid and reduced with an excess of tin for 2.5 hours at 55°–58°. The excess of hydrochloric acid was then removed by evaporation at 100°, the tin salt dissolved in cold water and the tin precipitated as sulphide with hydrogen sulphide. When this solution was concentrated we obtained a crystalline hydrochloride, which was identified as a salt of *p*-aminophenylethylamine. It was extremely soluble in cold water and was purified for analysis by crystallization from a mixture of alcohol and ether. It separated as a granular powder which had no definite melting point but decomposed from 270°–280°, according to the rate of heating. The base separates as an oil when the salt is treated with alkali. Analysis:

0.1267 gram substance gave 0.1611 gram AgCl.

	Calculated for		
	$C_8H_{14}N_2Cl_2$.	$C_8H_{14}N_2Cl_2.H_2O$.	Found.
Cl	33.48	31.27	31.45

Platinum Salt.—This was prepared by adding hydrochlorplatinic acid to an alcoholic solution of the hydrochloride. It separated in clusters of sharp-edged prisms which had no definite melting point. Analysis:

	Calculated for $(C_8H_{14}N_2Cl_2)_2.2PtCl_4$.	Found.
Pt	35.6	35.1

Picrate.—Crystallizes from hot water in needlelike prisms which melt at 223°–224° with effervescence. Analysis (Kjeldahl):

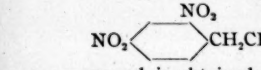
	Calculated for $C_8H_{14}N_2Cl_2(C_6H_2O_7N_3)_2$.	Found.
N	18.91	18.90

*Acetyl-*p*-aminophenylethylamine,* $(p)NH_2C_6H_4CH_2CH_2NHCOCH_3$.—A quantitative yield of this base is obtained by reduction of the corresponding nitro derivative, in dilute alcohol, with aluminium amalgam. After filtration from the aluminium hydroxide and evaporation of the alcohol the base was obtained as a thick syrup, which did

not solidify after standing at ordinary temperature for 10 hours. It dissolved in hydrochloric acid, giving a hygroscopic dihydrochloride, which was extremely soluble in water and absolute alcohol. It crystallizes from a hot, saturated, aqueous solution in clusters of radiating prisms. When heated in a capillary tube the salt sintered above 170° and decomposed at 191°–192° with violent effervescence. The salt was dried for analysis in a desiccator over concentrated sulphuric acid and potassium hydroxide. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{14}ON_2(HCl)_2$.	Found.
N	11.1	10.91

Acetyl-2,4 dinitrophenylethylamine,



$NO_2C_6H_3(NO_2)CH_2CH_2NHCOCH_3$.—A good yield of this compound is obtained by dissolving 2.0 grams of acetylphenylethylamine or acetyl-*p*-nitrophenylethylamine in a mixture of 6 cc. of concentrated sulphuric and nitric (sp. gr. 1.51) acids. After allowing to stand for a few minutes *only* at 10°–20° the acid solution is then diluted with ice water and neutralized at a low temperature with ammonia. The dinitro derivative separates as a yellow oil which soon crystallizes. It is extremely soluble in alcohol and moderately soluble in boiling water. It was purified for analysis by recrystallization from hot water and separated, on cooling, as an oil which soon crystallized in characteristic prisms melting at 97°–98° to a yellow oil with no effervescence. The compound is basic and dissolves at once in dilute hydrochloric acid. Analysis (Kjeldahl):

	Calculated for		Found.
	$C_{10}H_{11}O_5N_3$.	$C_8H_7O_4N_3$.	
N	16.60	19.90	16.68

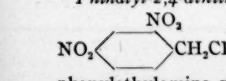
Oxidation of Acetyl-2,4-dinitrophenylethylamine with Potassium Dichromate.—Nine-tenths of a gram of the dinitro compound was dissolved in a solution of 3.2 grams of potassium dichromate in 6.5 cc. of concentrated sulphuric acid and heated for 12 hours at 100°. On cooling, a crystalline substance

separated, which was purified by crystallization from hot water. It separated on cooling in long, yellow needles melting at 177°–179°. The compound was soluble in alkalis and was identified as 2,4-dinitrobenzoic acid.[1] A mixture of the oxidation product and Kahlbaum's 2,4-dinitrobenzoic acid melted sharply at 180°.

Phthalylphenylethylamine, $C_6H_5CH_2CH_2N(CO)_2C_6H_4$, was prepared by carefully mixing 15 grams of phenylethylamine with the calculated amount of finely pulverized phthalic anhydride (20 grams) and heating in an oil bath at 140°–150° for about 2 hours. It crystallizes from boiling alcohol in well-developed prisms or tables which melt at 133°. The yield of pure amide was 26 grams. Analysis (Kjeldahl):

	Calculated for $C_{16}H_{13}O_2N$.	Found.
N	5.57	5.30

Phthalyl-2,4-dinitrophenylethylamine,



$CH_2CH_2N(CO)_2C_6H_4$.—Five grams of phthalylphenylethylamine were dissolved in 20 cc. of nitric acid (sp. gr. 1.51), cooled below 10°, and the mixture allowed to stand for 30 minutes. It was then poured upon crushed ice when the dinitro compound separated in colorless, prismatic crystals. The amide is insoluble in water and alcohol, but soluble in boiling glacial acetic acid, from which it separates, on cooling, in rhombic tables melting at 215°. The weight of the crude dinitro compound was 4.5 grams, corresponding to 70 per cent. of the theoretical yield. Analysis (Kjeldahl):

	Calculated for		Found.
	$C_{16}H_{12}O_4N_2$.	$C_{16}H_{11}O_6N_3$.	
N	9.46	12.2	11.8

When the acid filtrate above was concentrated we obtained a crystalline product which crystallized from glacial acetic acid in needles melting at 170°–176°. This substance was apparently a mixture of the dinitro and mononitro amides

[1] *Loc. cit.*

and melted after several recrystallizations from alcohol and acetic acid at 178°–180°. A nitrogen determination (Kjeldahl) gave 10.3 per cent., while the calculated value for a mononitro compound is 9.46 per cent. It was not investigated further.

p-*Nitrophenylethylamine*, $(p)NO_2C_6H_4CH_2CH_2NH_2$. — This amine was obtained in the form of its hydrobromide and hydrochloride by hydrolysis of acetyl-*p*-nitrophenylethylamine with hydrobromic and hydrochloric acids, respectively. Forty-two grams of the acetyl compound were dissolved in 70 cc. of hydrobromic acid (sp. gr. 1.48) and the solution heated to boiling, in an oil bath, for 3 hours. When the excess of hydrobromic acid was removed by evaporation, we obtained 46 grams of the hydrobromide, or 92.5 per cent. of the theoretical yield. This salt is very soluble in water and crystallizes from boiling 95 per cent. alcohol in plates, which melt at 218°–219° to a dark oil. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_2N_2.HBr$.	Found.
N	11.33	11.6

A theoretical yield of the *hydrochloride* was obtained by heating the amide with concentrated hydrochloric acid at 140°–150°. This salt is extremely soluble in water. It was purified for analysis by crystallization from absolute alcohol and separated, on cooling, in characteristic, tabular crystals or prisms which melted at 212°–214° to a clear oil with violent effervescence. Analysis:

0.1552 gram substance gave 0.1120 gram AgCl.

	Calculated for $C_8H_{10}O_2N_2.HCl$.	Found.
Cl	17.52	17.7

p-*Nitrophenylethylamine* separated as a yellow oil when its salts were decomposed by alkali. It is a strong base which absorbs carbon dioxide from the air, giving a crystalline carbonate. The base cannot be distilled with steam. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_2N_2$.	Found.
N	16.86	16.5

Platinum Salt.—This crystallizes from hot water in prismatic crystals, which decompose at 223°.

1-Phenyl-2-(p-Nitrophenylethyl)thiourea, $C_6H_5NHCSNHCH_2CH_2C_6H_4NO_2(p)$.—From phenyl isothiocyanate and *p*-nitrophenylethylamine. It crystallizes from alcohol in stout prisms which melt at 136° to an oil. Analysis (Kjeldahl):

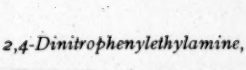
	Calculated for $C_{15}H_{15}O_2N_3S$.	Found.
N	13·95	13·70

Benzenesulphone-p-nitrophenylethylamine, $C_6H_5SO_2NHCH_2CH_2C_5H_4NO_2(p)$.—This was prepared by the action of benzenesulphone chloride on *p*-nitrophenylethylamine in presence of sodium hydroxide. It is soluble in warm sodium hydroxide solution, giving a sodium salt which crystallizes, on cooling, in plates. The amide is soluble in benzene and insoluble in water. It crystallizes from alcohol in prisms which melt at 107°–108°. Nitrogen determinations on the air-dried material indicated that the amide contained alcohol of crystallization (Kjeldahl):

	Calculated for		Found.	
	$C_{14}H_{14}O_4N_2S$.	$C_{14}H_{14}O_4N_2S.C_2H_5OH$.	I.	II.
N	9·15	7·9	7·75	7·53

Benzenesulphonemethyl-p-nitrophenylethylamine, $C_6H_5SO_2N(CH_3)CH_2CH_2C_6H_4NO_2(p)$.—Ten grams of benzenesulphone-*p*-nitrophenylethylamine and 1 gram of sodium hydroxide were dissolved in 75 cc. of alcohol and 7 grams of methyl iodide added to the solution. After heating on the steam bath for 4 hours, the alcohol was evaporated and the product obtained triturated with cold water to remove sodium iodide. The amide was insoluble in water but soluble in boiling alcohol. It separated, on cooling, in rectangular crystals which melted at 98° to an oil. A mixture of this compound and benzenesulphone-*p*-nitrophenylethylamine melted at 74°–98°. The yield was 9 grams. The compound was insoluble in sodium hydroxide solution. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{16}O_4N_2S$.	Found.
N	8·7	8·30

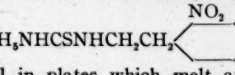
2,4-Dinitrophenylethylamine,  .—The hydrochloride of this base is obtained by hydrolysis of acetyl-2,4-dinitrophenylethylamine, or the corresponding phthalyl compound, with hydrochloric acid, at 140°–150°. It is very soluble in water and moderately soluble in cold alcohol. It crystallizes from absolute alcohol in prisms which melt at 197°–198° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_4N_3Cl$.	Found.
N	16.97	16.89

The free base is precipitated as a heavy oil when sodium hydroxide is added to an aqueous solution of the hydrochloride.

Picrate.—Crystallizes from hot water in needles which melt at 159° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{14}H_{12}O_{11}N_6$.	Found.
N	19.0	18.80

1-Phenyl-2-(2,4-dinitrophenylethyl)thiourea,  .—Crystallizes from alcohol in plates which melt at 128°. It is difficultly soluble in benzene. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{14}O_4N_4S$.	Found.
N	16.1	15.75

NEW HAVEN, CONN.,
JANUARY 1, 1910.

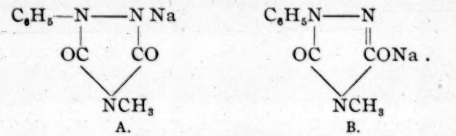
ON THE APPLICATION OF PHYSICAL-CHEMICAL METHODS TO DETERMINE THE MECHANISM OF ORGANIC REACTIONS.

BY ARTHUR MICHAEL.

S. F. Acree and his coworkers have published a number of interesting investigations on phenylurazole and its deriva-

tives, from the experimental results of which the former chemist has drawn the following conclusions regarding the mechanism of tautomeric reactions:

"A salt of a tautomeric compound reacts with an alkyl halide, or other reagent, and forms two compounds, because the tautomeric salt is really a mixture of two tautomeric salts in equilibrium, each of which reacts with the alkyl halide in independent side reactions."[1] Thus the sodium derivative of 4-methylphenylurazole exists in solution as



A. B.

When an alkyl halide, or other organic reagent, reacts on such tautomeric salts in solution the reaction takes place practically completely between the anions of the two salts and the halide.[2]

On the basis of these generalizations, Acree discusses the several hypotheses which have been previously advanced to explain merotropic reactions,[3] and endeavors to show that they are in opposition to the experimental results which he has obtained in the investigation of the urazoles. The principal reasons given by Acree for assuming that the reactions proceed through the union of the anions of the urazole salts with the halide are as follows:

1. The free urazoles should give much lower velocity constants than their salts in solutions of the same concentration, since "organic acids are, as a rule, much less dissociated than their sodium salts."[4] This explanation is untenable, since it leads to the conclusion that the velocity of alkylation of organic acids should increase with their acidity constants, while,

[1] THIS JOURNAL, **37**, 78.

[2] *Ibid.*, **37**, 83. Ber. d. chem. Ges., **41**, 3207.

[3] In a merotropic reaction a substance which exists only in one form passes over into a *derivative* of an isomeric form. See Michael: J. prakt. Chem., **42**, 19; **44**, 125. THIS JOURNAL, **14**, 487. Ann. Chem. (Liebig), **363**, 20.

[4] Acree and Shadinger: THIS JOURNAL, **39**, 234.

as is well known, the alkylation of organic acids cannot be realized under such conditions, quite irrespective of the value of such constants. The comparison between organic acids, on the one hand, and urazoles and their salts, on the other, is unwarranted. The free urazoles are amphoteric substances[1] and that they react with alkyl halides is due to their basic and not to their acidic nature. As bases they must show an affinity for halhydric acid, and the formation of the alkyl derivatives is due to this affinity.

2. If the reactions are ionic and independent of the nature of the cation, the metallic urazole salts should give "reaction constants, the values of which are directly proportional to the percentages of dissociation of the salts at the same concentration."[2] In confirmation of this statement, the following data are to be found in Acree's papers: The values of k_1 for the action of ethyl iodide (0.2 N at 25°) on the sodium, barium and magnesium derivatives of phenylthiourazole are 0.36, 0.32 and 0.42. Acree remarks that the velocity constants of the sodium and barium salts "agree very well with the amount of dissociation, but the constant for magnesium 1-phenyl-3-thiourazole is apparently high."[3] In 0.2 N solutions of sodium and barium nitrates (at 18°) the salts are dissociated 78.7 and 60.9 per cent., whereas the relation calculated from Acree's experiments is 78.7 and 71.1. With the sodium and magnesium salts, Acree's results would lead to dissociation values the exact reverse of those actually found. In a later paper,[4] the values of k_1 for the action of ethyl iodide on the sodium, potassium, barium and zinc salts of 4-methylphenylurazole (3 N in 40 per cent. alcohol at 60°) were found to be 0.42, 0.36, 0.28 and 0.05. If we take into consideration that the percentage dissociation of sodium and potassium nitrates in 0.2 N solution is practically the same (78.7), that of the barium salt is 60.9, and those of sodium, potassium and zinc chlorides (0.2 N) are 81.1, 83.6 and 69.1,

[1] Acree: THIS JOURNAL, **38**, 346. Ber. d. chem. Ges., **41**, 3225.
[2] Acree and Shadinger: THIS JOURNAL, **39**, 232.
[3] *Ibid.*, 234.
[4] Acree: Ber. d. chem. Ges., **41**, 3215.

it is obvious that the results[1] obtained by Acree in the alkylation experiments serve as better evidence against, than for, the assumption that such reactions are ionic in character.

3. If the reactions are ionic, the addition of an electrolyte to the urazole-alkyl halide solution should partially suppress the ionization of the urazole salts and therefore cause a decrease in the values of the velocity constants.[2] The nature of the influence that neutral salts exert on the velocity constants in certain reactions is still a matter of speculation.[3] Acree's argument is based on the original explanation given by Arrhenius, but this investigator, at least in the classical instance of the influence exerted by neutral salts on a mixture of acid and sucrose, has apparently abandoned the hypothesis and now assumes that the alteration in the reaction velocity is due to the added electrolyte increasing the osmotic pressure of the sugar.[4] As a means for determining the mechanism of organic reactions, this method has led to results so contradictory among themselves that its importance as a basis for theorizing cannot be regarded as in any sense satisfactory. Thus, Schwab[5] and Senter[6] have shown that neutral electrolytes, when added to a mixture of sodium chloracetate and sodium hydroxide, greatly increase the reaction velocity constants, and Steger[7] has further shown that sodium iodide exerts no influence on the reaction velocity between *o*-dinitrobenzene and sodium ethylate. Acree[8] himself

[1] The above values are calculated on the assumption that complete ionization is practically reached at a dilution of 10,000 liters. Kohlrausch (Z. Elektrochem, **1907**, 342) has recently discussed this subject.

[2] Acree and Shadinger: THIS JOURNAL, **39**, 231.

[3] See Caldwell: P. Roy. Soc., **78**, 272. Geffcken: Z. physik. Chem., **49**, 257. Senter: J. Chem. Soc., **91**, 462.

[4] See Senter: *Ibid.*, **91**, 463.

[5] van't Hoff: Etudes, 26 and 113.

[6] J. Chem. Soc., **91**, 470.

[7] Z. physik. Chem., **49**, 333.

[8] Ber. d. chem. Ges., **41**, 3219. Acree attempts to explain this discrepancy by assuming that sodium iodide acts catalytically, but the salts in question are too nearly related chemically for this suggestion to be accepted as valid. The majority of the concordant results were obtained with the thiourazoles, but since organic thio derivatives have a marked tendency to unite with various substances, to form double compounds, it is evident that the first step in investigations of this nature is to ascertain whether the added electrolyte can unite with any of the components of the system to form such a product, since its formation must result in a change of energy, which in turn must necessarily affect the velocity constant.

shows, that potassium iodide decreases the value with sodium 4-methylphenylurazole, while sodium iodide increases it.

There thus appears to be no valid evidence in support of Acree's view that the reactions in question proceed through union of the anions of the salts with the alkyl halides. Acree[1] considers as Comstock's theory the view that when silver and potassium salts lead to isomeric alkyl derivatives these salts have structures corresponding to those of the alkyl derivatives. This view dates back, however, years before the appearance of Comstock's papers; indeed 22 years ago the writer,[2] in discussing this subject, assumed it was generally known, and showed that even at that time it was not tenable. Acree[3] believes that this view is improbable in the urazole reactions, but considers it a valid explanation in those reactions where only one of the possible isomers is formed. The proof put forward by the writer[4] in 1888, that the structure of a metallic salt does not necessarily follow from that of the alkyl derivative obtained from it, has already, for some years, met with general acceptance, and the older view, incorrectly denoted by Acree as "Comstock's theory," has been abandoned.

How incompatible the latter view is with the law of entropy is evident from the following example. Potassium benzamide gives *N*-, and the silver derivative *O*-alkylbenzamide; hence, according to the hypothesis in question, the first salt is a *N*- and the latter an *O*-derivative. Now, the adoption of these structures involves the assumption that the substance containing potassium is derived from the neutral, or practically neutral, keto form, notwithstanding that the potassium in such a structure would contain an enormous amount of free *chemical* energy and that its affinity for the oxygen is very much greater than for the nitrogen. On the other hand, the very weakly positive silver ($AgOH = 1 \times 10^{-4}$) is assumed to exist in the enolic, *i. e.*, acidic, form, although it

[1] This Journal, **37**, 78. Ber. d. chem. Ges., **41**, 3204.

[2] J. prakt. Chem., N. F., **37**, 520. All that Comstock did was to apply this view (at one time very generally accepted) to explain his own experimental results.

[3] Ber. d. chem. Ges., **41**, 3205.

[4] J. prakt. Chem., N. F., **37**, 473.

may be made from the potassium derivative by double decomposition, and its affinity for oxygen is much less than that of potassium.

"Wheeler's theory" to explain tautomeric reactions is quoted by Acree[1] as follows: "When one salt yields with a certain reagent two products, one is formed directly and the second by rearrangement of the first." Wheeler,[2] in 1899, generalized an observation that Knorr[3] had previously made with more complicated derivatives, *viz.*, certain derivatives of the imidoester type, which are stable under conditions of temperature where addition of an alkyl iodide causes a rearrangement into the *N*-derivatives. Wheeler explained this change in two ways: the halogen of the halide united with the carbon, and the alkyl with the nitrogen of the —C = NH— group; or, the alkyl halide adds to the imido group to form an ammonium derivative; in either case the product thus formed breaks down into a *N*-alkyl derivative and alkyl halide. He concludes that "The tautomeric reaction in these cases, as in others, is undoubtedly nothing but a reaction by addition,"[4] but there is no indication in the papers of this investigator that this explanation was intended to serve as a general theory for tautomeric changes, as stated by Acree,[5] and it is so obviously impossible to use it for this purpose that the subject will not be discussed.

[1] THIS JOURNAL, **37**, 78. Ber. d. chem. Ges., **41**, 3205.

[2] THIS JOURNAL, **21**, 187; **23**, 135; **30**, 38.

[3] It appears to have escaped attention that a strict proof of the intermediate formation of an addition product in these rearrangements may be found in the earlier experiments of Knorr, who (Ber. d. chem. Ges., **30**, 929) showed that the O-*ethyl* derivative of α-quinoline is converted by methyl iodide, slowly in the cold, quickly and completely in the heat, into the N-*methyl* derivative. Later, Wheeler (THIS JOURNAL, **23**, 139) showed that when isobutylimidobenzoic ester is heated with methyl iodide it yields benzmethylamide. The fundamental reason for this rearrangement is the increase of entropy brought about when the *O*-derivative, which has the smaller heat of formation, passes over into the *N*-isomer. If we change the structure of these substances so as to decrease the chemical resistance to the change, or to increase the affinity of the migrating radical for the atom to which it wanders, which in the case of the imido esters is done by introducing an alkyl into the imido group—the rearrangement may be brought about more readily, *i. e.*, by heat alone (Wislicenus and Goldschmidt: Ber. d. chem. Ges., **33**, 1467). Thermochemical work is in progress for placing this view (which is applicable to every case of intramolecular rearrangement) on a better experimental basis than the data at hand afford.

[4] THIS JOURNAL, **21**, 187.

[5] Ber. d. chem. Ges., **41**, 3205.

"According to Nef's and Michael's addition theories, the salt has one structure,"[1] and is derived from the enolic form of the merotrope.[2] This theory assumes that, when such a salt yields two isomeric derivatives, one of them is formed by direct substitution of the metal and the other by the spontaneous decomposition of an intermediate addition product.

Acree[3] criticizes the "addition theory" as follows: "This theory demands that under the same conditions of solution all the different salts should give a mixture of esters in which the ratio of the *O*-ester to the *N*-ester is a constant," since the metallic ion should not affect the course of the reaction. Different urazole salts, however, "give widely different ratios of *O*-ester to *N*-ester, and hence Nef's and Michael's addition theories are inadequate."

This criticism is based on an inadequate knowledge of the "addition theory," and is not substantiated by Acree's ex-

[1] Acree: THIS JOURNAL, **37**, 81. In Acree's paper in the Ber. d. chem. Ges. (**41**, 3206) the statement is made that the addition theory was arrived at independently by Nef. This theory was published by the writer (J. prakt. Chem., N. F., **37**, 473) in 1888, and developed at that time so as to include practically all important tautomeric reactions known at that time. Three years later, Nef (Ann. Chem. (Liebig), **266**, 52) reproduced the writer's views; partially unchanged, partially in a slightly modified form. The changes which Nef made in this theory have never been accepted, and were untenable at the time of their publication (see THIS JOURNAL, **14**, 520). *Although Nef was thoroughly acquainted with the writer's paper, he failed to state that he was simply reproducing the ideas of another chemist, and, as his article was published in a widely read journal, it is sometimes believed that he really has some claim to the origination of the "addition theory."*

[2] This statement is quite as inaccurate as the above. The theory that merotropic keto derivatives, when converted into salts, become enol derivatives, was originated and widely developed by the writer in 1888, in the same paper as the "addition theory," and was only connected with it, inasmuch as the latter is necessary to explain the reactions of such enolic salts. During the succeeding four years (1892), *Nef persistently claimed that no structural change occurs in such reactions*, and then (Ann. Chem. (Liebig), **270**, 330) suddenly changed his opinion regarding the structure of the metallic derivatives of the nitroalkanes and accepted those which the writer (J. prakt. Chem., N. F., **37**, 507) had previously assigned to these salts. *Here, again, Nef used his method of silent appropriation. Although he now adopted the very principle, which only a year previously (Ibid.*, **266**, 56) *he had declared untenable, the reader is led to believe in this and in his subsequent papers* (see Claisen: *Ibid.*, **291**, 43, footnote) *that this idea originated with him.* While the writer consistently developed a general theory and showed its wide application and importance in organic reactions, the phenomenon remained a haphazard relation with Nef; thus acetacetic ester and hydrocyanic acid (see Michael and Hibbert: Ann. Chem. (Liebig), **364**, 70), as well as their sodium derivatives, are supposed to be enolic derivatives. The writer's views on this subject have been incorporated into accepted chemical theory, while those which may be said to belong to Nef have not been adopted.

[3] THIS JOURNAL, **37**, 82.

perimental results. The "addition theory" does not demand that under the same conditions of solution these metallic salts should give a constant ratio of *O*-to *N*-derivative, but is historically the first explanation why such a relation may depend on the metal in the salt; nor is it connected with the fact, as stated by Acree,[1] that in solutions these metallic salts contain the same anion. Furthermore, the results which Acree has obtained by using the same alkyl halide and those urazole salts which were under the same conditions in solution show a ratio between *N*- and *O*-alkyl derivative so closely together that, considering the rough method used in determining the ratios,[2] one cannot say with any certainty to what extent they differ. The silver salt alone gives a decidedly different ratio, but, as it is practically insoluble in the solvent employed, it cannot be considered as being "in the same condition of solution;" moreover, that silver salts often give different results is one of the oldest known facts in the field of tautomerism and one which the writer[3] explained by means of the "addition theory."

Addition was assumed to take place in two different ways: (*a*) When the substance contains, besides the metal, nitrogen or sulphur in a condition similar to that of these elements in ammonias or methyl sulphide, a substituted ammonium, or sulphonium, halide is primarily formed, which breaks down into a metallic halide and a merotropic alkyl nitrogen, or sulphur, derivative;[4] or, (*b*) in such compounds, where the addition of the reagent to a single unsaturated atom is constitutionally impossible, for instance with sodium acetacetic ester, $CH_3 - CONa = CH - COOC_2H_5$, addition takes place by breaking a double bond with subsequent breaking down of the addition product.[5] Acree,[6] in discussing the application of this theory to the alkylation of the urazoles, wrongly ascribes to it an addition of the parts of the halide "to the

[1] Ber. d. chem. Ges., **41**, 3207.
[2] *Ibid.*, **41**, 3223.
[3] J. prakt. Chem., N. F., **37**, 520 (1888).
[4] *Ibid.*, **37**, 508.
[5] *Ibid.*, 487.
[6] Ber. d. chem. Ges., **41**, 3207.

double bond between nitrogens and carbons;"[1] an assumption which is theoretically improbable and not supported by the properties of such substances. Acree has also overlooked the fact that the writer has been engaged for many years in subjecting the "addition theory" to that final test of all speculation, *viz.*, to experimental verification, and has obtained results[2] which have led him to modify the "addition theory" in its original form very materially and to endeavor to connect it with the law of entropy.

In considering the merotropic relations of the urazoles from the point of view of the present "addition theory," it will be assumed that a considerable change in the energy and affinity relations of atoms in these substances does not occur in the formation of the ring,[3] an assumption which appears probable from their properties. The discussion of the relations will therefore be based on the chemical nature of the two characteristic radicals contained in the urazoles; *viz.*, that of a symmetrical diacylphenylhydrazide, on the one hand, and that of an imide of a very weak dibasic acid on the other. The acid imides give enolic sodium derivatives, but, even with an imide of a strong dibasic acid, such salts are easily hydrolyzed by water. The phenylhydrazides also readily give enolic sodium derivatives, which show, however, a greater stability towards water. Phenylurazole may exist in a keto and in 3 mono-enolic forms:[4]

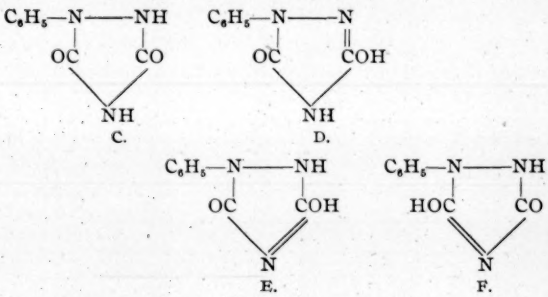
[1] THIS JOURNAL, **37**, 81.

[2] J. prakt. Chem., N. F., **60**, 316–325; **68**, 492. Ber. d. chem. Ges., **33**, 3731; **34**, 4028; **38**, 23, 1922, 2083, 2096, 3217. Ann. Chem. (Liebig), **363**, 66.

[3] J. prakt. Chem., N. F., **79**, 418.

[4] Acree (THIS JOURNAL, **38**, 1) has examined the behavior of phenylurazole, and certain of its derivatives, towards diazomethane in ether solution, and concludes that phenylurazole exists in such solution mainly as D (see next page) although this form is in equilibrium with E and F (perhaps also with the dienolic form) present in relatively small proportions. The discoverer of diazomethane, von Pechmann (Ber. d. chem. Ges., **30**, 646), proved that it is not a trustworthy reagent to distinguish between keto and enol derivatives, a view which has since been confirmed (Michael and Hibbert: Ann. Chem. (Liebig), **364**, 70).

Diazomethane has an extremely large content of free *chemical* energy, which gives it a great reactivity and enables it to perform a very considerable chemical work at ordinary temperature. The question, whether it will react to give a merotropic methyl derivative of the substance depends on the affinity of its methylene group to those atoms in the merotropic substance that may unite with it. Its great capacity for performing chemical work makes it powerful, however, in effecting rearrangements, if the affinity relations do not permit the formation of the methyl derivative corre-



It is apparent that D, which is the enolic form of the hydrazide radical, should represent the most acidic of the enolic structures; indeed, it has been proven experimentally by Acree and Shadinger[1] that the acidity constants of urazole derivatives of the type D are several hundred times greater than those of E and F. Since the chemical resistance to enolization by alkalies of imides and hydrazides is extremely slight, the keto form (C), when treated with aqueous alkali, in equivalent proportion, should contain the sodium deriva-

sponding to the structure of the tautomer under examination. Thus, von Pechmann showed that diazomethane converts acetacetic ester, which is a stable keto derivative, into the enolic β-methoxycrotonic ester; obviously because the negative influence of the azo group in the reagent and of the acetyl and carbethoxyl groups in the ester have greatly diminished the affinity of carbons in the two methylene groups. When this negative influence is less pronounced in the substance, as, for instance, in aldehyde, diazomethane is able to readily replace the hydrogen directly joined to carbon by methyl. Some chemists, H. Meyer (Monatsh., **25,** 1193), Peratoner and Palazzo (Centralb., **1908,** I, 21), and Acree have been misled by the great reactivity of diazomethane into believing that it can be successfully used as a tautomeric reagent, whereas it is debarred through this very property (see Michael and Smith: Ann. Chem. (Liebig), **363,** 39). Free phenylurazole, like free cyanic and cyanuric acids, is undoubtedly a keto derivative (C); the neutral, or almost neutral, character of these, and analogous, products in this condition shows that the molecule in this form is intramolecularly better neutralized than when it is in the acidic form, and that the E $\longrightarrow$ C rearrangement proceeds with increase of entropy. Like cyanic acid (see Wolgast: Diss., Leipzig, 1906), phenylurazole presents but slight chemical hindrance to enolization; even water, though so slightly basic, is able through mass action to convert them into acids which both have about the affinity constants of propionic acid. Cyanic acid has been proven to have the keto form in ether solution (Michael and Hibbert: Ann. Chem. (Liebig), **364,** 1291); in what forms the phenylurazole derivatives exist in such a solution may perhaps be determined by their behavior towards amines (Michael and Smith: *Ibid.*, **363,** 36).

[1] THIS JOURNAL, **39,** 124.

tives of the 3 enolic forms, but, according to the "principle of partition,"[1] the quantitative amounts should stand in a relation to the acidity constants of these forms; that is, the solution should contain a large amount of the metallic derivative of the relatively strongly acidic D and very little of those of the weakly acidic E and F forms. Even this does not completely exhaust the theoretical possibilities with phenylurazole, since the NH group in the various forms may exhibit a slight acidity, in which case *N*-sodium derivatives should exist in the solution, although it is safe to say that the actual amounts of such derivatives would be inappreciable. With 4- and 2-methyl-1-phenylurazole the relations are comparatively simple; in aqueous solution the first substance and caustic soda in equivalent amount should give almost entirely the *O*-sodium salt corresponding to the D form, and the second a mixture of *O*-salts corresponding to the enolic forms E and F. These conclusions are very different from those reached by Acree,[2] who believes, for instance, that the metallic derivatives of 4-methylphenylurazole are mixtures of the *N*- and *O*-forms, and that the percentage of the *O*-form decreases with the positivity of the metal. Thus, with the strongly positive sodium, there is more *N*- than *O*-, and with the weakly positive silver, there is more *O*- than *N*-salt. Acree[3] has proven that the 4-methylphenylurazole has in aqueous solution almost the activity constant ($K = 1.1 \times 10^{-5}$) of propionic acid, and now assumes that this acid is converted, on the addition of caustic soda, to a considerable extent into a sodium salt derived from a much less acidic form! These results are incompatible with one another and also stand in contradiction to the law of entropy. The energy required to overcome the chemical resistance to the formation of any possible isomeric form of the metallic derivative is invariably subordinate to the increase of entropy, due to the more perfect neutralization of the large amount of positive

[1] Michael: J. prakt. Chem., N. F., **60**, 339. Ber. d. chem. Ges., **39**, 2138–2156, 2570, 2569; **40**, 140. When the "principle of partition" was first developed (J. prakt. Chem., N. F., **60**, 339) it was stated as a wide generalization of that involved in Thomson's "avidity principle."

[2] THIS JOURNAL, **37**, 83. Ber. d. chem. Ges., **41**, 3201, 3216.

[3] THIS JOURNAL, **39**, 126.

energy in the alkali or alkali metal by the most acidic form of the merotrope which can be formed.[1]

The fallacy in Acree's reasoning is obvious; it leads, for instance, to the impossible conclusion that in an aqueous solution of a very strong and an extremely weak acid, with insufficient alkali present for complete neutralization, we have much salt of the weak and only little of that of the strong acid. Equally fallacious is Acree's second conclusion, *viz.*, that the proportion of *O*-salt is greater with silver than with sodium; this would imply, to take a simple illustration, that a mixture of a very strong and a weak base, in solution with insufficient acetic acid for neutralization, would contain more acetate of the weak than of the strong base!

The merotropic relations of phenylurazole are evidently extremely complicated, and those of the 4- and 2-methyl derivatives which are much simpler and present the further advantage that Acree has studied their reactions quantitatively, will be discussed instead. Formanilide will be used as the standard of comparison for the hydrazide group, as the merotropic reactions of phenylhydrazides have not been sufficiently examined for our purpose.

The formation of ammonium salts depends on nitrogen having an affinity for hydrogen sufficient to give a certain stability to the ammonium radical, thus enabling the hydrogens to neutralize through the nitrogen and through space the negative energy of the halogen.[2] Since this process of neutralization takes place largely spatially, there must be bound *chemical* force in an ammonium halide between the hydrogens, as well as between the nitrogen and the halogen.[3] If we in-

[1] This important law has been proven experimentally. Michael: Ber. d. chem. Ges., **33**, 3731; **38**, 22, 1922.

[2] Michael: Ber.d. chem. Ges., **39**, 2792, footnote. THIS JOURNAL, **41**, 126.

[3] It is customary to assume, in the addition of hydrochloric acid or methyl iodide to ammonia, that there is a complete separation of the parts of the addenda; an assumption which is unproven and theoretically very improbable. Since bound *chemical* force exists between the hydrogen or methyl and the halogen in the addition products, the bound *chemical* force between the hydrogen or methyl and the halogen decreases during the process of addition only to the extent that it exists in the addition product, *i. e.*, an actual separation of the addenda into two parts does not take place. This conception of addition applies to all cases where bound *chemical* force exists between the parts of the addenda after the addition has taken place. That rearrangements like iso into tertiary butyl bromide do not, as will be experimentally shown in a later paper, proceed by dissociation and subsequent addition, but through the undissociated molecule agrees with this view.

troduce a formyl radical in place of a hydrogen in phenylammonium iodide, we not only reduce the affinity of the remaining hydrogens, and the nitrogen, for the halogen, but also the neutralizing power of the ammonium radical; for this reason such salts show an extremely slight stability and the free amides are unable to overcome the considerable chemical resistance which accompanies the addition of an alkyl halide to an ammonia derivative.

What is the mechanism of the action of sodium on formanilide, and how does the introduction of the metal change the energy and affinity relations of those elements that may unite directly with the alkyl group, *i. e.*, of nitrogen and oxygen?

The sodium has afforded to it two points of attack: one on the nitrogen and one on the oxygen of the anilide, and, in either case, it has to overcome the resistance involved in the separation of hydrogen from the nitrogen.[1] The two factors that determine the chemical action, *i. e.*, the affinity of nitrogen and oxygen for sodium and the free *chemical* energy in these atoms, exist evidently much more developed in the oxygen than in the nitrogen of the anilide and these relations permit the direct formation of *O*-sodium formanilide, which represents the maximum entropy of the system:

$$2C_6H_5.NH.\overset{H}{\underset{|}{C}} : O + Na_2 = 2C_6H_5.N : \overset{H}{\underset{|}{C}}.ONa + H_2.$$

The energy and affinity changes that occur with the introduction of sodium into formanilide are as follows: as a derivative of a very weak acidic substance, *i. e.*, of enol formanilide, the positive chemical energy of sodium is only imperfectly neutralized, and, as the metal enters into direct chemical union with the oxygen, that element must lose much of its free *chemical* energy in the process. On the other hand, the bound *chemical* force, which in the anilide held the nitrogen and the subsequently liberated hydrogen in chemical union, has been partially transformed in the salt into free *chemical*

[1] Michael: Ber. d. chem. Ges., **34**, 3731; **38**, 1933.

energy in the nitrogen. Further, not only has the introduction of sodium increased the free *chemical* energy of the nitrogen, and decreased that of the oxygen, but it has converted the negative —CHO (formyl) into the strongly positive CHONa group and, thereby, greatly increased the affinity of the nitrogen for alkyl. For these reasons the "polymolecule," which is first formed in the action of methyl iodide on sodium formanilide, decomposes with formation of the *N*-derivative; and as this has a greater heat of formation than the isomeric *O*-product, the maximum entropy of the system is thus directly realized:[1]

$$\begin{array}{l} C_6H_5.N \longleftarrow CH_3 \\ \quad\| \qquad\quad | \\ HCONa \longrightarrow I \end{array} = \begin{array}{l} C_6H_5.N.CH_3 \\ \quad | \\ \quad HCO \end{array} + NaI.$$

By introducing into sodium formanilide the weakly positive silver ($AgOH = 1 \times 10^{-4}$), in place of the very strongly positive sodium, a relative change in the affinity relations of the nitrogen and oxygen for methyl in favor of the latter element takes place. The silver is much less able than the sodium to neutralize the effect caused by the introduction of formyl into aniline and the free *chemical* energy in the oxygen. The formation of a *N*-derivative is prevented by the alteration in the affinity values; owing to the second and the strong affinity between silver and iodine, the reaction proceeds with the formation of the *O*-derivative:

$$\begin{array}{l} C_6H_5.N:CH.O \longleftarrow CH_3 \\ \quad\quad | \qquad\quad | \\ \quad\quad Ag \longrightarrow I \end{array} = C_6H_5N:CHOCH_3 + AgI.$$

With methyl iodide and sodium 4-methylphenylurazole, 96–97 per cent., and with ethyl iodide, 92–94 per cent., of *N*-alkyl derivative is formed.[2] These results are not only

[1] There appears to be no valid reason for assuming the intermediate formation of a substituted alkylammonium iodide in this reaction. It is more probable that the sodium, which is the most powerful positive force in the salt, acts directly in effecting the endothermic separation of the iodine from the methyl. The reason why methyl iodide reacts with such difficulty on neutral sodium salts of organic acids is that the free *chemical* energy in the metal and in the two oxygens of the carboxyl group has been largely converted into bound *chemical* energy and heat in the formation of the salt.

[2] Acree: Ber. d. chem. Ges., **41**, 3227.

in conformity with the "addition theory," but are also in close agreement with a principle developed some years ago,[1] *viz.*, that when alkyl halides react with salts to form mixtures of isomeric alkyl derivatives, the more positive the alkyl radical is, *i. e.*, the greater its tendency towards a metallic character, the greater proportion of that isomer will be formed whose structure is analogous to that of the metallic salt.[2] As far as is known, methyl and ethyl iodides react with silver formanilide to form exclusively *O*-alkyl derivatives; with silver 4-methylphenylurazole the first reagent gives a mixture of *N*- and *O*-derivatives in about equal proportions, while with the latter about 38 per cent. of *N*- and 62 per cent. of *O*-product[3] is obtained. The imido group in formanilide shows no capacity to add alkyl halides, while that in the hydrazide radical of the urazole does, and this tendency should increase somewhat with the introduction of the silver radical. These merotropic relations in the case of the silver urazoles are very similar to those of silver nitrite; in each case the silver salt of a weak acid, containing an unsaturated nitrogen, is extremely sensitive to a change in the alkyl radical and, here too, in agreement with the theory, the proportion of *O*-derivative increases with the relative positivity of the alkyl group.[4]

Similar results have been obtained by Acree[5] in the alkylation of the salts of 2-methylphenylurazole, where the acid imide group is involved in the reactions. The results obtained from the sodium salt and methyl and ethyl iodides are practically the same as those from the 4-methyl derivative; with the silver salt the first halide gives 87–90 per cent. and the second 48–50 per cent. of *O*-derivative. If, as is probable, the additive power of the imido group for alkyl halide in the acid imide group is less than that in the hydrazide radical, the proportion of *O*- to *N*-alkyl derivative should be greater

[1] Michael: J. prakt. Chem., N. F., **60**, 323.

[2] This is due to a change in the affinity relation favoring oxygen with increasing metallic character of the radical and to the fact that the difference between the heats of formation of the isomeric derivatives becomes less.

[3] Acree: Ber. d. chem. Ges., **41**, 3229.

[4] Von Meyer: Ann. Chem. (Liebig), **175**, 88. Tschenriak: *Ibid.*, **182**, 158.

[5] Ber. d. chem. Ges., **41**, 3232.

with the 2- than with 4-methylphenylurazole. This is indeed the case with ethyl iodide, but with methyl iodide it is almost the same with both urazoles, and this is the only one of Acree's results that awaits a satisfactory explanation.[1]

We pass now to a discussion of Acree's own hypothesis as an explanation of merotropic reactions. The small velocity constant of certain merotropes, in comparison to the large value of their metallic derivatives, is explained as follows: "The weakly acid tautomeric amides, acetacetic ester, etc., react, as a rule, very slowly with alkyl halides, acid chlorides, etc., at ordinary temperature, because these weak acids furnish few *anions* of the tautomeric forms to react with the alkyl halides. The addition of bases, such as pyridine, alkalies or other metallic hydroxides, or sodium ethylate, causes an increase in the reaction velocity because the base forms, to a greater or less extent, depending on the strength of the acid or base, tautomeric salts of the amide, acetacetic ester, etc. These salts, because they are more highly ionized than the acid, furnish the solution with a greater concentration of the anions of the 2 or more tautomeric forms and hence the reaction velocity is increased."[2]

Acetacetic ester is ionized to a slight extent in solution ($K = 2 \times 10^{-11}$),[3] as well as the acid amides, although the latter undoubtedly to a far less degree. They do not, as stated by Acree, react with alkyl halides at ordinary temperature, or at any temperature, in the sense implied in the above statement of Acree's. There is, furthermore, no relation between the extent to which enolic substances yield anions in solution and their capability of yielding alkyl derivatives, since the weakest and the strongest enols are inert in this respect. Nor is the behavior of these substances towards the acyl chlorides in agreement with Acree's views; acetacetic ester is very slightly ionized in aqueous solution and does not react at all to form an acetyl derivative, while the

[1] The acid imido group in the urazoles should show more capacity for adding alkyl halide than that in the imide of an ordinary dibasic organic acid, since it has the basic phenylhydrazine, whereas the latter has a neutral hydrocarbon, as the mother substance.

[2] Science, **30**, 21. Ber. d. chem. Ges., **41**, 3199.

[3] Goldschmidt and Scholz: Ber. d. chem. Ges., **40**, 624.

amines, which are undoubtedly still less ionized, react very readily.

To explain the formation of two isomers in the alkylation of certain metallic derivatives, Acree[1] assumes that they consist of a mixture of two tautomeric salts, and when the equilibrium of these salts is disturbed by chemical reaction—certain reagents showing a selective preference for one or the other form—it is immediately reestablished. Thus, sodium acetacetic ester is represented by the formula

$$CH_3.CONa : CH.COOC_2H_5 \rightleftarrows CH_3.CO.CHNa.COOC_2H_5,$$[2]

and gives an *O*- or *C*-derivative according to the selective taste of the reagent employed. This view represents a long step backwards, even when compared with the original conception as to the nature of the structural changes that take place in the conversion of acetacetic ester into its sodium derivative. Geuther supposed the formulas

$$CH_3.COH : CH.COOC_2H_5 \text{ and } CH_3.CONa : CH.COOC_2H_5$$

to represent the structures of acetacetic ester and its sodium derivative, while, up to 1888, the generally accepted Frankland-Wislicenus view assumed the forms

$$CH_3.CO.CH_2.COOC_2H_5 \text{ and } CH_3.CO.CHNa.COOC_2H_5.$$

The writer[3] then showed that the chemical relations of these substances could be explained only by accepting the formula

$$CH_3.CO.CH_2.COOC_2H_5,$$

for the ester, and

$$CH_3.CONa : CH.COOC_2H_5$$

for the salt. After explaining why a compound having a structure represented by

$$CH_3.CO.CHNa.COOC_2H_5$$

cannot be stable, but must undergo a spontaneous rearrangement, the metal passing over to oxygen, the following statement was made: "Es lässt sich aber nicht verkennen, dass

[1] This Journal, **37**, 78. Ber. d. chem. Ges., **41**, 3210.

[2] This Journal, **37**, 77.

[3] J. prakt. Chem., N. F., **37**, 473. This Journal, **10**, 158; **14**, 481.

eigentlich zwei isomere, stabile Natriumacetessigäther aus der unbeständigen Verbindung entstehen sollten, da der stark negative Carbonylsauerstoff des Carbäthoxyls gewiss eine bedeutende Verwandschaf tauf das Natrium ausübt. Demnach sollte neben der Verbindung

$$CH_3.CONa : CH.COOC_2H_5$$

auch eine gewisse Menge von

$$CH_3.CO.CH : C(ONa)OC_2H_5$$

entstehen."[1] That an alcoholic solution of sodium acetacetic ester must contain some of the latter sodium derivative will be obvious on considering that malonic ester is readily converted by sodium ethylate into the enolic sodium derivative, and that acetacetic ester may be looked upon as derived from malonic ester by replacing one of the carbethoxyl groups by the more acidic acetyl group. It follows, therefore, from the principle of partition, that an alcoholic solution of sodium acetacetic ester is a mixture of the above enolic derivatives, in which the $CH_3.CONa : CH.COOC_2H_5$ form greatly preponderates, since the enol form from which it is derived is much more acidic than the enol form of the malonic ester type. A chemical system can change spontaneously only when it is accompanied by an increase of entropy, and it is extremely improbable that the equation

$$CH_3.CO.CH_2.COOC_2H_5 + C_2H_5ONa = CH_3.CO—CHNa.COOC_2H_5 + C_2H_5OH$$

represents such a change. Even if we assume the formation of such a *C*-sodium derivative, its concentration would be exceedingly small and only if the two enolic sodium acetacetic esters were inert toward the reagent would we be justified in assuming that the reaction proceeds through the salt with the smallest concentration. Owing to the very slight acidity of the enol acetacetic esters, the content of free *chemical* energy in their sodium derivatives must be very great and it is safe to say that, even with a reagent so comparatively inert

[1] J. prakt. Chem., N. F., **37**, 488.

as alkyl iodide,[1] the reaction would proceed practically through the enolic salts, notwithstanding the presence of a trace of the keto salt and the fact that the latter would have a still larger content of energy.

However, a theory that proposes to explain the behavior of the metallic derivatives of merotropes should at least be able to connect the chemical character of the substances with those of the reagents, as well as be in harmony with the course of the reactions. The application of Acree's views to the acetacetic ester reactions leads to inconsistent conclusions. For example, ethyl iodide, chlorcarbonic ester and acetyl chloride react with sodium acetacetic ester, with formation of a *C*-, a mixture containing much *O*- and little *C*-, and a *C*-derivative, the reactivity of the reagents following the order stated above.[2] In explaining the urazole reactions, Acree assumes that the ratio of the tautomeric alkyl derivatives formed in the reaction stands in a relation to the proportion of the tautomeric salts originally present. From this point of view, the behavior of ethyl iodide and acetyl chloride proves that sodium acetacetic ester is a *C*-derivative, while, according to the action of chlorcarbonic ester, it is present largely in the *O*-form. To state, as Acree does, that certain reagents exert a "selective affinity" for one or the other tautomeric form, partakes more of tautology than of a scientific explanation, but this view also leads to conclusions that are contradictory among themselves. Thus, according to Acree's view, ethyl iodide "selects" the *C*-sodium acetacetic ester, while chlorcarbonic ester (a much more reactive reagent) favors the *O*-derivative, notwithstanding that the latter contains less positive energy than the *C*-salt; finally, acetyl chloride, which is still more reactive, "selects" the *C*-salt.[3]

Besides the objections mentioned above, Acree believes that his experimental results, while they support his own views, disprove the "addition theory" in a number of other respects. From the latter hypothesis it would have been

[1] See Michael: Ber. d. chem. Ges., **38**, 3223.

[2] Ber. d. chem. Ges., **41**, 3216.

[3] For explanations of these reactions, based on the law of entropy, see Michael: Ber. d. chem. Ges., **38**, 1922, 2083, 2097, 3217. J. prakt Chem., N. F., **73**, 542.

possible to predict the possibility of a change in the ratio of *N*- to *O*-alkylphenylurazole by changing the nature of the solvent. Thus, with silver 4-methylphenylurazole and ethyl iodide in ether, alcohol, acetone and water, 35, 33, 39 and 37 per cent. of the *N*-derivative are formed.[1] Acree states that these slight differences may be due to changes caused by the solvent in the relative reactivities which the two anions show towards the halide, or that the value of K_3 changes with the solvent, a view which appears more a restatement of the facts in other terms than a satisfactory explanation. When we consider that Menschutkin[2] has shown that the additive power of triethylamine for alkyl halide depends on the solvent present, and that the ratio of *N*-derivatives formed in the urazole reaction depends on the additive power of the nitrogen in question, it is apparent that, with a substance so sensitive to changes as the silver urazole derivative, it would have been possible to predict Acree's results from the "addition theory."

The constancy of the ratio of *N*- to *O*-alkylurazoles in the action of ethyl iodide on potassium and silver 4-methylphenylurazole between 22° and 90° is an objection to the "addition theory."[3] It is in agreement with Acree's views and for the following reasons: "Der negative Temperaturkoeffizient für die Dissoziation der beiden tautomeren Salze ist, wie bereits Jones and West, wie auch Noyes und Coolridge, nachgewiesen haben, nur sehr klein und ausserdem bei allen Salzen nahezu der gleiche."[4] Acree's results show, however, that the proportion of *N*-derivative, instead of being constant, varies up to 5 per cent., that is, the effect of change in temperature is greater than that caused by change in solvent, which Acree, on the same page in his paper, had emphasized as important. Furthermore, the change in the dissociation of tautomeric salts with temperature has never been investigated[5] and there is no evidence at hand which enables us to say whether the tem-

[1] Acree: Ber. d. chem. Ges., **41**, 3216.
[2] Z. physik. Chem., **6**, 41.
[3] Acree: THIS JOURNAL, **37**, 82.
[4] Ber. d. chem. Ges., **41**, 3216.
[5] The statement quoted above from Acree's paper leads one to believe that tautomeric derivatives have been examined by Jones and West and Noyes and Coolridge, but this is not the case.

perature coefficients of conductivity of two products so different in their chemical character as the sodium *O*- and *N*-urazoles must be is so small as Acree assumes. Why it should follow from the "addition theory" that the above changes in temperature should cause a greater variation in the *N*- and *O*-ratios than Acree found, the writer is unable to understand and he cannot consider these results an objection to that theory.

According to Acree,[1] a change in the concentration of the substances in these urazole reactions does not cause an appreciable variation in the ratio of *N*- to *O*-derivative; thus, with sodium 4-methylphenylurazole and ethyl iodide, or allyl iodide, although the concentration was decreased four times the ratio remained constant at 94 : 6 and 98 : 2. This result also agrees with his views, since the *N*- and *O*-sodium salts have similar dissociation values. Only with allyl iodide are experimental data quoted in Acree's paper;[2] in one experiment with 10 parts dilute alcohol 97.7 per cent., and in 4 others with 20 parts of solvent 96.7 to 99.1 per cent. *N*-derivative were formed. Acree[3] has described his method for determining the above ratio, according to which the product of alkylation is subjected to a long series of operations, the insoluble residue finally obtained being the *O*-derivative. As the total product in the above experiments was about 0.2 gram, and the final insoluble product about 0.004 gram, it is difficult to understand how Acree could venture to draw the conclusion stated above from such slight experimental material. Acree's statement,[4] moreover, that the *N*- and *O*-sodium urazoles should have similar dissociation values does not agree with the chemical character of derivatives analogous to such substances. The first salt, being derived from the keto form, should be largely hydrolyzed in dilute alcoholic solution, while the second, which is derived from an acid having about the acidity constant of propionic acid, should be only slightly hydrolyzed. It is also obvious that such experi-

[1] Ber. d. chem. Ges., **41**, 3218.
[2] *Ibid.*, 3228.
[3] *Ibid.*, 3223.
[4] *Ibid.*, 3218.

mental results do not in any way disprove the "addition theory," as claimed by Acree, nor does it follow from this theory that a change in concentration should cause an appreciable variation in the *N*- to *O*-ratio.[1]

In support of his views, Acree quotes a number of investigations by other chemists, but the confirmation is more apparent than real, since some of the results are inaccurately stated, and the others are inapplicable to illustrate "the use of selective reagents in proving the presence of two tautomeric salts."[2] Hantzsch's work on phenylnitromethane, and Wislicenus' on formylphenylacetic ester are selected. According to Acree,[3] Hantzsch showed that the first substance dissolves in alkali, forming, besides $C_6H_5CH : NO(ONa)$, a small proportion of $C_6H_5CHNaNO_2$. In reality Hantzsch did not prove the presence of a *C*-derivative but emphasizes that the solution contains only *O*-salt.[4] Acree also states that if the salts of the tautomeric phenylnitromethanes "exist in tautomeric forms in solution," then "we should be able to select an acid weak enough to precipitate the more weakly acid tautomeric form," but not the stronger acid form, while "a strong mineral acid would precipitate both tautomers."[5] Hantzsch's experiments "amply verify this point. Carbonic acid precipitates the true phenylnitromethane from solutions of its alkali salts, whereas strong acids precipitate the more strongly acid isonitro form, nearly pure."[6] There is nothing in Hantzsch's researches, or in his theoretical views, to justify such statements. Hantzsch[7] states that the keto form is a

[1] Acree (Ber. d. chem. Ges., **41,** 3217; THIS JOURNAL, **37,** 85) also claims that his views enable one to "predict" that different alkyl halides should show varying reaction coefficients and that the proportion of *N*- to *O*-derivative may depend on the nature of the halide. These are subjects which have often been discussed previously (see J. prakt. Chem., N. F., **37,** 521; **60,** 319, 368) and the writer fails to see that Acree has in any way contributed to a better understanding of them, or why it should be necessary to "predict" a relation that previous investigators have already put on an experimental basis.

[2] THIS JOURNAL, **37,** 76.

[3] *Ibid.*, **38,** 33.

[4] Ber. d. chem. Ges., **32,** 2257.

[5] THIS JOURNAL, **37,** 76.

[6] *Ibid.*, 77.

[7] Ber. d. chem. Ges., **29,** 2257.

neutral substance, and explains the behavior of the alkali salt towards carbonic acid and strong acids in a manner which is not open to doubt, *viz.*, carbonic acid, in comparison to the isonitro derivative, is so weak an acid that only traces of the first body are liberated, which isomerize to the neutral form; as the equilibrium between carbonic acid and the iso acid is thereby disturbed, the reaction proceeds with further separation of traces of the isonitro body and simultaneous isomerization. On the other hand, strong acids precipitate the isonitro acid practically completely, and so nearly instantaneously that it has not time to isomerize.

Equally inaccurate and misleading are Acree's statements with regard to formylphenylacetic ester. W. Wislicenus[1] originally regarded the two modifications of this substance, also those of certain of their metallic derivatives, as tautomeric; Hantzsch[2] accepted tautomerism for the ester and suggested stereoisomerism for the salts, while Knorr[3] assumed the esters as well as the salts to be isomers. Wislicenus[4] subsequently gave up his first view in favor of that of Hantzsch. The writer[5] showed later that the solid modification (72°) of Wislicenus is a mixture of two desmotropes (50° and 100°) and that the three desmotropes are all enolic. The liquid form was shown to be stable towards carbonic acid but not towards dilute sulphuric acid, while the modification melting at 50° is stable towards dilute and that at 100° stable towards strong sulphuric acid, which behavior explains why the desmotropic form precipitated from the salts depends on the acid and its concentration. The above results obviously give no support to Acree's views, or to his statement that the salts are tautomeric and are present as such in equilibrium in the solution.

Acree[6] indeed believes that with "proper solvents and experimental conditions both forms" of the tautomeric salts

[1] Ann. Chem. (Liebig), **291**, 147.
[2] Ber. d. chem. Ges., **29**, 2266.
[3] Ann. Chem. (Liebig), **306**, 377, footnote.
[4] *Ibid.*, **313**, 34.
[5] Ber. d. chem. Ges., **39**, 203.
[6] THIS JOURNAL, **37**, 84.

that exist in solution could probably be isolated, and, in support of this opinion, quotes, besides the research of Wislicenus mentioned above, that of Hantzsch and also of Titherly. Hantzsch[1] found that cyanuric acid, which is a keto derivative, dissolves in soda to form the merotropic *O*-salt. If this solution is kept at 0°, and a soluble mercuric salt added, an *O*-mercury salt is precipitated, while at 100° we have a *N*-mercury salt formed, and between these temperatures a mixture of the isomeric salts results. The affinity relations of sodium and of mercury towards oxygen and towards nitrogen are exactly reversed; that is, with sodium there is a decrease from oxygen to nitrogen, while with mercury there is an increase. That the *O*-sodium salt at 0° gives an *O*-mercury, and at 100° a *N*-salt, shows that at the higher temperature the *O*-derivative is able to rearrange itself to the modification representing the maximum condition of entropy, and this fact offers no support to Acree's view, according to which the sodium salt in solution is a mixture of both forms.

Titherly[2] found that when caustic soda is added to an aqueous solution of silver nitrate and benzamide a white, stable silver derivative is precipitated, but if silver nitrate is added to sodium benzamide, both substances in alcoholic solution, an orange precipitate is formed, which quickly decomposes. Similar results were obtained with acetamide; the orange salt in the latter case is slightly more stable, however, and it was possible to make a silver determination, which gave a result agreeing approximately with that required for silver acetamide. These observations show that stable, white silver derivatives of known composition and structure, and very unstable, yellow products of unknown composition, structure and purity have been obtained, but they do not confirm Acree's views in any way. Acree[3] finds confirmation of his theoretical views, also, in the organic researches of Hantzsch and Caldwell and Scholl and Steinkopf, as well as in the physical-chemical researches of Burke and Donnan, Slator, Senter,

[1] Ber. d. chem. Ges., **38,** 2722.
[2] J. Chem. Soc., **71,** 486; **79,** 408.
[3] Ber. d. chem. Ges., **41,** 3210.

Euler and Hecht, Conrad and Brückner. These investigations are supposed to furnish experimental proof that organic reactions may be ionic in character, and as they are exerting an influence on organic theory, the writer deems it of importance to discuss them from the point of view of an organic chemist.

Hantzsch and Caldwell[1] treated silver nitroform with methyl iodide at —75° and obtained an addition product of the formula $C(NO_2)_3Ag.2CH_3I$. This substance is decomposed by water, and by nearly absolute alcohol, at —10°, into nitroform; and when suspended in indifferent solvents it decomposes into trinitroethane (*C*-derivative) and silver iodide. Silver nitroform, which exists only in a hydrated condition, dissolves readily in ether and the solution gives, with methyl iodide, the *C*-derivative, with a trace of nitroform. Hantzsch and Caldwell explain these results by assuming that silver nitroform in ether solution reacts only in the ionic condition; to the nitroform ion ($C(NO_2)_3$) methyl may add in two directions *i. e.*, either to oxgyen or to carbon, and the *C*-derivative is formed because it is the more stable of the two products. The addition product ($C(NO_2)_3Ag.2CH_3I$)[2] can only decompose intramolecularly, *i. e.*, as an undissociated complex, and, since the silver is joined to oxygen, the *O*-methyl derivative ($C(NO_2)_2=NO(OCH_3)$) is formed. The latter body is decomposed by water into nitroform and methyl alcohol, but in its absence it isomerizes to the *C*-derivative. These explanations are open to very serious objections. If the formation of the *C*-derivative depends on the existence of the nitroform anion, then potassium nitroform, which must be more dissociated in solution, should also give the same substance, but Hantzsch and Rinckenberger[3] showed that no reaction takes place. Further, if we accept the view that it is the nitroform anion which reacts in the formation of the methyl derivative, the further assumption that methyl may

[1] Ber. d. chem. Ges., **39**, 2473.

[2] The formation of this substance at a low temperature and its behavior at a somewhat higher temperature is an exceedingly interesting, experimental confirmation of the view, that in every reaction the primary step is the formation of a "polymolecule."

[3] Ber. d. chem. Ges., **33**, 628.

add *a priori* either to oxygen or to carbon is extremely improbable. The effect of 3 such negative radicals as NO_2, and which are joined directly to carbon, would be to greatly reduce the affinity of this carbon for methyl.[1] Thus, silver oxalacetic ester ($C_2H_5OOC.COAg$: $CH.COOC_2H_5$) and ethyl iodide give solely an *O*-ethyl derivative;[2] that is, even the radicals $COOC_2H_5$ and $CH.COOC_2H_5$ reduce the affinity of the Δ^β—C (C of the CH group) to such an extent that the reaction proceeds not by addition but by the direct substitution of silver. These organic radicals, however, exert, in comparison to NO_2, a very weakly negative influence, and it is therefore safe to say that the assumption that the nitroform anion[3] can unite with methyl to form a *C*-derivative is untenable. For the same reason, *viz.*, the reduction of the affinity of the unsaturated carbon for methyl due to the strongly negative radicals, a spontaneous isomerization,

$$C(NO_2)_2NO(OCH_3) \longrightarrow CH_3.C(NO_2)_3,$$

cannot be considered at all likely; nor is it probable that *O*-methylnitroform would be decomposed by almost absolute methyl alcohol at —100° in a short time into nitroform and methyl alcohol.[4] In view of these serious objections, Hantzsch's assumption that the alkylation proceeds through the anion of the salt cannot be considered at all probable. Hantzsch accepts the keto structure of nitroform as representing a neutral substance, but, if we lay stress on the great negative influence which must be exerted by 3 nitro groups on the methane hydrogen, it seems more probable that it represents an acidic substance. When we consider, further, the weakly basic properties of silver hydroxide ($AgOH = 1 \times 10^{-4}$) and that silver shows a decided affinity for carbon when the latter element is in a relatively negative condition,[5] it seems by no means unlikely that the intramolecular, atomic neutralization in $Ag.C(NO_2)_3$ is better than that in $C(NO_2)_3$:

[1] See J. prakt. Chem., N. F., **60**, 291, VIII. Ber. d. chem. Ges., **39**, 2142.

[2] Nef: Ann. d. Chem., **276**, 227.

[3] Hantzsch and Caldwell assume $C(NO_2)_3$ as the nitroform anion, but if silver nitroform has the O-structure the anion should be represented by $C(NO_2)_2N(O)O^-$.

[4] The analogous alkyl nitrates are quite stable towards alcohol.

[5] For instance in acetylene derivatives.

N(OAg). In this case the rearrangement of the *O*- into the *C*-derivative would represent an increase of entropy, and the stable silver derivative which is known contains the metal joined to carbon.[1] With such a derivative the action of methyl iodide alone, or in presence of a solvent that cannot furnish hydrogen for forming hydriodic acid, must lead to the formation of *C*-methylnitroform. Silver nitroform, like other silver salts, has a strong affinity for hydriodic acid, and, in the presence of solvents that can furnish hydrogen, for instance water or alcohol, the reaction may proceed more easily by the elimination of that acid from the halide and water, or alcohol, in which case nitroform would be set free, than through the direct substitution of silver.[2]

Scholl and Steinkopf[3] examined the reaction between silver nitrate and iodomethylcyanide. These substances unite to form a fairly stable addition product ($NCCH_2I,AgONO_2$), which is decomposed by boiling water into its components, and on dry distillation into silver iodide and the compound $NC.CH_2.ONO_2$. Here we have another interesting experimental verification of the theory that reactions proceed through the "polymolecule" phase.[4] That in the dry distillation of such a product the halogen unites with silver and is replaced by the nitrate group and that this double compound is decomposed by water into its components is certainly no evidence in favor of the reaction being ionic.[5]

Burke and Donnan[6] have studied the action of alcoholic silver nitrate on alkyl iodides. These reactions, as Nef[7] had previously shown, are very complicated; the metal in the nitrate may be replaced by alkyl, or, owing to the affinity of silver nitrate for hydriodic acid, alkenes may be formed,

[1] Ley and Kissel (Ber. d. chem. Ges., **32**, 1366) proved that mercuric nitroform in a solid state, or dissolved in indifferent solvents, is a *C*-derivative; in alcohol and water it is at least partially the *O*-salt.

[2] Nef (Ann. Chem. (Liebig), **309**, 140) showed that silver nitrate and alkyl halides in absolute alcoholic solution react to give, besides esters, free nitric acid to a very considerable extent. If *C*-silver, like *C*-mercury nitroform, is converted by water, or alcohol, into the *O*-salt, it would be structurally analogous to silver nitrate.

[3] Ber. d. chem. Ges., **39**, 4393.

[4] *Ibid.*, **34**, 4028; **39**, 2140. THIS JOURNAL, **39**, 3; **41**, 120.

[5] Acree: Ber. d. chem. Ges., **41**, 3214.

[6] J. Chem. Soc., **85**, 555.

[7] Ann. Chem. (Liebig), **309**, 140.

which, in presence of the nitric acid set free, may unite with the alcohols to form mixed ethers. The velocity constant is, therefore, dependent on the following relations; firstly, the relative ease of replacement of the iodine in the alkyl iodides by the nitrate group; secondly, the relative ease of elimination of hydriodic acid from the alkyl iodides by alcoholic silver nitrate. A further factor enters into the relative proportions of the reaction products, *viz.*, the relative facility with which the nascent, unsaturated alkenes may unite with the alcohol used as a solvent. The reaction between alcoholic silver nitrate and alkyl iodide forms, therefore, a complex subject for an investigation of the relations between the structure of the alkyl group and the process of substitution on the one hand, and that of elimination, complicated by that of addition, on the other. It is obvious that the determination of velocity constants in such complicated reactions cannot give us an insight into their mechanism, since it is impossible to determine the part that the several different processes involved play in the final results. Indeed, Burke and Donnan[1] were unable to explain the variations in the values of K and state "in particular the assumption that it is the silver ions, which take part in the fundamental reaction which regulates the speed, does not appear to offer a simple explanation."

Slator[2] has examined the action of alkyl halides on metallic thiosulphates and considers that he has obtained experimental evidence to show that in this reaction the anions of the salt react with undissociated halide. It is a well-known fact that alkyl halides react only with considerable difficulty on neutral salts of the alkali group, while in salts showing an alkaline reaction the reaction takes place the more readily, the more

[1] J. Chem. Soc., **85**, 588. It is evident that in such a mixed reaction the relations between the relative reactivity of the alkyl iodides must be different from those obtained in reactions that proceed solely through direct substitution of the halogen, and Burke and Donnan's results show this to be the case. The relations between the above 3 fundamental organic processes and the structures of organic radicals united with the halogen have been partially developed (Michael: J. prakt. Chem., N. F., **60**, 372–384, 409–420; **68**, 499. Ber. d. chem. Ges., **34**, 4215; **42**, 3174, footnote), and the writer will take the occasion of publishing experimental work on the relation of chemical structure to real substitution, and to that of apparent substitution, through elimination and addition to the unsaturated substance thus formed, to develop more fully the theoretical aspect of this very important subject.

[2] J. Chem. Soc., **85**, 1286; **87**, 481.

free *chemical* energy is contained in the metal. Notwithstanding that sodium thiosulphate is a neutral salt, Bunte[1] found that, when it is heated in aqueous solution with so comparatively inert a halide as ethyl bromide, the sodium joined to sulphur is extremely easily replaced by ethyl. Slator found, in the action of ethyl bromacetate on sodium thiosulphate, that with the sodium salt the reaction proceeds very readily, but the addition of small quantities of silver nitrate to the mixture decreases the reactivity to an extent corresponding to the formation of a complex salt, $Na_3Ag(S_2O_3)_2$,[2] which shows a reactivity so small as to be negligible in comparison with that of sodium thiosulphate. Slator[3] believes that the above "complex salt is partially dissociated according to the equation

$$Na_3Ag(S_2O_3)_2 \rightleftarrows Na_2S_2O_3 + NaAgS_2O_3,$$

and that the reaction depends on the presence of a small quantity of uncombined sodium thiosulphate."[3] He also believes that "the ions $Ag(S_2O_3)'''$, AgS_2O_3', and the corresponding undissociated salts either do not react or react with only a relatively much smaller velocity, and sees in the fact that addition of silver nitrate to sodium thiosulphate lowers the reactivity so decidedly "strong evidence in support of the view that the reaction is primarily connected with the S_2O_3'' ion."

Slator's experimental results with the thiosulphates show an order of reactivity exactly the reverse of that of the sodium and silver salts of all acids not containing the metal joined directly to sulphur, since, with such salts, it is the silver that reacts with far greater velocity than the somewhat more ionized sodium salt. It is, therefore, obviously wrong to assume the reaction is ionic with the thiosulphate, and we must seek another explanation for the apparently abnormal reactivity of these salts.

In the first paper[4] on the "addition theory," attention was

[1] Ber. d. chem. Ges., **7**, 646.

[2] Such a salt has not been isolated. The salt $NaAgS_2O_3$ dissolves in sodium thiosulphate to form the compound $Ag_2S_2O_3.2Na_2S_2O_3$. The latter salt is quite stable and as its formation proceeds with loss of free *chemical* energy, it should show a smaller reactivity towards alkyl halide than sodium thiosulphate.

[3] J. Chem. Soc., **87**, 490.

[4] J. prakt. Chem., N. F., **37**, 508–511.

directed to the instantaneous and violent addition of methyl iodide to methyl sulphide; it was pointed out that if sulphur in an organic compound exists in a similar condition of "polarity" (it was then called "positive" sulphur) it should also show an additive power for alkyl halide, more or less developed according to its condition of positivity, and should lead to the formation of unstable, metallic sulphinium derivatives. Thus the reaction between methyl iodide and sodium thiocyanate was represented[1] by the equation

$$\mathrm{Na{-}S{-}CN + CH_3I = Na{-}\overset{\mathrm{I}}{\underset{\mathrm{CH_3}}{S}}{-}CN = CH_3{-}S{-}CN + NaI.}$$

Although thiocyanic acid must have a very considerable affinity constant, its alkali salts react with alkyl halides with great readiness, while the silver salt is comparatively inert.[2] Here we have the same relations as Slator found with the corresponding thiosulphates. Silver is very weakly positive ($AgOH = 1 \times 10^{-4}$) in comparison with an alkali metal; by replacing the strongly positive sodium by the weakly positive silver, the sulphur in the thiocyanate and thiosulphate loses its additive power for alkyl halide. The reaction, therefore, proceeds by direct substitution of the silver, which, although it goes much faster than the direct substitution of sodium, is considerably slower than the addition process. Slator proved that the reactivity of thiosulphates does not vary greatly when very positive metals, *i. e.*, potassium, sodium, barium or strontium, are present in the salts and that such solutions in reacting with organic halides follow the law of mass action. His assumption that these reactions proceed through union of the anions of the salts with the halides stands in direct contradiction to the properties of these and similar compounds, whereas the chemical explanation just given is in agreement and explains, in a satisfactory manner, the effect of adding silver nitrate.

Senter[3] has published an interesting investigation on the

[1] J. prakt. Chem., N. F., **37**, 509.
[2] Von Meyer: Ann. Chem. (Liebig), **171**, 47.
[3] J. Chem. Soc., **91**, 460.

hydrolytic decomposition of chloracetic acid by water, and of its sodium salt by water and by caustic alkali, as well as on the influence of neutral salts on the velocity constants of these reactions. The reaction velocity of the system, acid and water, is but little affected by neutral salts, or by hydrochloric acid, which leads Senter to the conclusion that it is the undissociated acid that mainly undergoes decomposition. With sodium chloracetate and water, Senter finds that in very dilute solutions the velocity is proportional to the concentration, while it increases more rapidly than the concentration in stronger solutions; sodium chloride exerts a considerable effect, but potassium chloride and nitrate only a slight, negligible, retarding influence. The change with concentration agrees with the assumption that the undissociated salt is acted on, but this view is incompatible with the strictly monomolecular character of this change in very dilute solutions and Senter[1] thinks his experimental results are best explained by assuming the main reaction in dilute solution to take place between $CH_2Cl.COO'$ ions and nonionized water, while in more concentrated solutions the reaction of the undissociated sodium salt becomes of importance. Senter[2] explains the results obtained from sodium chloracetate and alkali by a similar assumption, only here the hydroxyl ions enter into the reaction. He also finds that sodium chloracetate is hydrolyzed only ten times more rapidly by 0.1 N sodium hydroxide than by water, and that the addition of neutral salts to the acetate-alkali system accelerates the velocity constant. These results are, as Senter[3] observed, in striking contrast to those obtained in other systems; thus, in the hydrolysis of esters, the reaction is enormously accelerated by alkali, and the addition of neutral salts decreases the constants. It is evident that results which show evidence of electrolytes reacting in an undissociated condition in aqueous solution, or, in that or a dissociated condition varying with the dilution, and which in part are so contradictory to the ionic point of view, do not

[1] J. Chem. Soc., **91**, 471.
[2] *Ibid.*, **95**, 1828.
[3] *Ibid.*, **91**, 474.

justify Acree[1] in claiming them as a support to the hypothesis that alkylations proceed under all conditions through union of the anions with the organic halide. Senter assumes that water, or alkali, acts on sodium chloracetate by directly replacing the halogen by hydroxyl. The fact that dry sodium chloracetate is decomposed at a moderate heat into glycolide and sodium chloride[2] indicates the existence of a decided affinity between the halogen and the metal. Owing to the resistance connected with the formation of a four-ring, *i. e.*, the β-lactone, the reaction proceeds through interaction of two molecules, forming in glycolide a six-ring derivative.[3] But if this affinity between metal and halogen comes into play in the presence of water, with its assistance the direct, intramolecular formation of sodium chloride is not only possible, but would probably proceed easily, as under such conditions glycollic acid may be formed:

$$\begin{array}{l} Cl\text{——}CH_2 \leftarrow OH \\ \downarrow \quad | \quad\quad | \\ NaO\text{—}CO \leftarrow H \end{array} = \begin{array}{l} CH_2OH \\ | \\ COOH \end{array} + NaCl.$$

It follows from this interpretation that the more highly ionized the salt is, *i. e.*, the more dilute the solution, the larger must be the proportion of the chemical change that takes place in the $ClCH_2\text{-}COO'$ ions; the comparatively slight increase in the reaction velocity by addition of caustic alkali is also consonant with it. It is probable, however, that, even in undissociated sodium chloracetate the direct replacement of halogen by hydroxyl proceeds, to a certain extent, simultaneously with the process just described and that the relative proportion between the two processes increases in favor of the first, when alkali instead of water is employed.

Euler[4] has examined the reaction between silver nitrate and chloracetic acid, and its salts, and that between silver

[1] Ber. d. chem. Ges., **41**, 3210.

[2] Kekulé: Ann. Chem. (Liebig), **106**, 288. Norton and Tscherniak: Bull. Soc. Chim., **30**, 102. Polyglycolide was formed, but as Bischoff and Walden (Ann. Chem. (Liebig), **279**, 46) subsequently showed that glycolide is formed by heating sodium bromacetate *in vacuo* and that it goes over on heating into polyglycolides, it seems probable that the latter is always the primary product.

[3] Michael: J. prakt. Chem., N. F., **60**, 336.

[4] Ber. d. chem. Ges., **39**, 2726.

nitrate and ethyl bromide. The velocity constant of chloracetic acid and silver nitrate is the same in 45 per cent. alcohol as in water. Euler[1] considers this result surprising, since the dissociation values differ considerably in these solvents; it is indeed difficult to reconcile the result with the view that the reaction is ionic. The velocity constant for sodium chloracetate and silver nitrate is much greater than when the free acid instead of the salt is used, while that with ethyl chloracetate is only one-half of that with the free acid. Euler assumes that the reaction between chloracetic acid and silver nitrate is represented by the equation

$$ClCH_2.COOH + AgONO_2 + H_2O = HOCH_2.COOH + AgCl + HONO_2,$$

and believes his results are best explained by supposing that in this, and in similar reactions, where one of the substances is largely in an ionic condition, the substitution proceeds through a complex ion of the type $\overset{+}{A}g.BrC_2H_5$. He thus explains the decrease in velocity when chloracetic ester instead of the free acid is used and its increase by using the sodium salt instead of the latter substance.

The first chemical change that takes place in an aqueous solution of chloracetic acid and silver nitrate is the formation of a certain quantity of silver chloracetate and nitric acid and the amount of the organic silver salt must stand in a relation to the acidity constants of chloracetic and nitric acids. It is a characteristic property of silver salts of organic halogen fatty acids to decompose extremely easily into silver halide and organic products, corresponding to the nature of the acid used.

The decomposition of silver chloracetate was first studied by Beckurts and Otto,[2] who found that in concentrated solution silver chloride and glycollic acid are very readily formed, and that the velocity of this reaction decreases with dilution. In striking contrast to this instability of the silver salt is the

[1] Ber. d. chem. Ges., **39**, 2729.

[2] *Ibid.*, **14**, 576. The dry silver salt decomposed at about 70° into silver chloride and glycolide.

comparative great stability of the corresponding sodium derivative,[1] and as the latter salt is undoubtedly dissociated in solution to a greater extent than the former, it would seem as if the dominating factor on which the instability of the silver salt depends can hardly be the formation of chloracetic ions. If the silver chloracetate formed on mixing chloracetic acid and silver nitrate decomposes much faster intramolecularly, *i. e.*, through direct union of the halogen with the metal, than the change represented by the above equation—and this can hardly be doubted—then the decomposition will proceed more or less completely in the first named manner. From this point of view, the use of sodium chloracetate, instead of the free acid, with silver nitrate must increase the reaction velocity enormously as the concentration of the silver chloracetate is greatly increased by the change. Euler's explanation of the decrease ensuing when the ester, instead of acid, is used is open to grave objections; it is not known whether chloracetic ester is capable of forming chloracetic ions at all, and, if so, their concentration must be inconsiderable in comparison with that of the free acid, whereas the velocity is only decreased one-half. According to the above point of view, silver chloracetate can be formed only indirectly from the ester, *i. e.*, from the acid formed through hydrolysis; it is likely, however, that the reaction proceeds partially in this way and partially by direct substitution of the halogen.

The interesting observation of Beckurts and Otto that the stability of silver chloracetate is greater in dilute than in concentrated solution, was made the subject of a quantitative investigation by Kastle.[2] This chemist found, for instance, that, at 100°, in a 0.09 N solution, 43 per cent. was decomposed in one hour, while with a 0.00015 N solution only 3 per cent. was decomposed. Ostwald[3] remarked, regarding the results, that they afford evidence of an intramolecular decomposition,

[1] Quantitative data with bromacetic acid are given in Senter's recent paper (J. Chem. Soc., **95**, 1835). In 0.1 N solutions the velocity for bromacetic acid and silver nitrate is 63 times greater than that for sodium bromacetate. For silver bromacetate the difference should be still greater.

[2] THIS JOURNAL, **14**, 586.

[3] Z. physik. Chem., **11**, 431.

since increasing dissociation develops greater stability, which agreed with the view advocated here. Euler's conclusions are based on imperfect assumptions regarding the manner in which the reactions proceed, and all chemical evidence agrees much better with the conclusion that the reactions involved represent not ionic but molecular changes.[1]

Finally, Acree[2] finds confirmation of the view that alkylation reactions proceed by union of the anions of the salt with the alkyl halide in the investigations of Hecht, Conrad and Brückner[3] on the formation of ethers from alcoholates and alkyl halides. These reactions were discussed from the ionic standpoint by Steger,[4] and later very thoroughly by Burke and Donnan,[5] who observe that "the explanation of these anomalies proposed by Steger, based on assumptions concerning the ionization of the sodium alkyl oxide and alkyl iodide in alcoholic solution, does not appear to hold good if the ordinary law of equilibrium is assumed."[6] The writer does not believe that the above researches permit of any legitimate conclusions being drawn with regard to the mechanism of these reactions. How complicated, and how little adapted this physico-chemical method is to throw light on the subject is evident from a research by de Bruyn and Steger,[7]

[1] Acree (THIS JOURNAL, **39,** 243) has criticized Euler's view on the ground that addition of potassium iodide to a solution of caustic potash and ethyl iodide should cause an increase in the concentration of the complex cations, $C_2H_5I.K^+$, and therefore increase the velocity constant of the reaction. Acree and Shadinger (*Ibid.*, **39,** 256) showed, however, that potassium iodide causes a decrease in the constant. Euler used $C_2H_5I.Ag^+$ as a symbol for a chemical type and confirms (Ber. d. chem. Ges., **39,** 2726) Schwab's previous observation, that addition of sodium chloride increases the velocity constant of caustic soda and sodium chloracetate. Are we to suppose from these results that the first reaction proceeds according to Acree's, and the latter according to Euler's views? In view of the irregularity in the results obtained by addition of neutral salts to systems containing organic halides and of the fact that the reason why they are sometimes inert, and sometimes exert an influence in one or the other direction, is so little understood, it is indeed surprising that results obtained by this method should be used as a basis for theorizing on the mechanism of organic reactions.

[2] Ber. d. chem. Ges., **41,** 3210.

[3] Z. physik. Chem., **4,** 273. 631; **5,** 289.

[4] Rec. Trav. Chim., **18,** 13.

[5] J. Chem. Soc., **88,** 581.

[6] *Ibid.*, 588.

[7] Z. physik. Chem., **49,** 336. See Tymstra Bz.: *Ibid.*, 346.

who have shown that addition of water to alcoholic solutions of the following systems,

I. $C_2H_5ONa + CH_3I$,

II. $CH_3ONa + CH_3I$,

III. $CH_3ONa + C_2H_5I$,

IV. $C_2H_5ONa + C_2H_5I$,

effects a decrease of the velocity constant in I; an increase up to 30 per cent. water, and above that a decrease, in II; a regular decrease in III; and a decrease up to 30 per cent. water, and then no further change, in IV. Here we have four systems which, chemically, are strictly analogous; if the reactions are ionic the addition of water should increase dissociation and consequently the velocity of reactions in each case. Yet the influence of water is different in each of the four systems, and in none of them does it conform to the requirements of the ionic theory. Until these anomalies are satisfactorily explained, it is a travesty on science to indulge in speculations about the mechanism of these reactions from the ionic point of view.

The writer has entered, in some detail, into the application of certain physical-chemical methods, which have been used with success in the examination of dilute solutions of inorganic electrolytes, to organic reactions, where at least one of the constituents is practically a nonelectrolyte, in the belief that the time has come to protest against the reckless theorizing on results obtained by these methods in which some enthusiastic followers of the ionic hypothesis have indulged as well as against their indifference to the results obtained in other ways and the ignoring by them of the chemical aspects of the problems. In the following statement regarding physical-chemical organic research, the writer, at all events, agrees with Acree:[1] "The worker who would do great service in this branch of science must have *as the great essential* such a broad and deep knowledge of organic chemistry that he can recognize wrong interpretations of reaction mechanisms almost by intuition; he must not make wrong postulations

[1] Science, **30**, 625 (1909).

regarding reactions." It would seem as if, in the researches discussed in this paper, Acree has not been altogether successful in his endeavors to realize these admirable ideals; for imperfect and incorrect representations of the views and results of other chemists certainly do not indicate "a broad and deep knowledge." Acree's own interpretations of reaction mechanisms, and some of those he favors, are plainly untenable, and there is no lack of "wrong postulations." The results obtained by him in the alkylation of urazole derivatives show that these reactions proceed in conformity with the law of mass action, *but do not warrant any of his conclusions regarding the mechanism of these, or of other reactions of tautomeric substances, nor do they stand in opposition to the "addition theory," but are further evidence in its favor, and of the necessity of founding the theory of organic chemistry on the law of entropy.*

ON THE REACTIONS OF DIAZOALKYLS WITH 1-PHENYL-2-METHYLURAZOLE.

[FIFTEENTH COMMUNICATION ON URAZOLES.]

By Sidney Nirdlinger and S. F. Acree.

(We are indebted to the Carnegie Institution of Washington for aid in our researches on tautomerism.)

The efforts to find the exact position of the two acid hydrogen atoms of phenylurazole[1] have shown that this compound is to be classed, from a theoretical point of view, among the most interesting and important of all tautomeric substances. The presence of two movable hydrogen atoms and the consequent possibilities of obtaining a large number of isomeric derivatives, each of which can be estimated quantitatively under easily regulated conditions, has made possible a quantitative study of the tautomeric phenomena presented, and the results have an important bearing on the question of tautomerism in general.

From a quantitative study of the reactions of the salts of phenylurazole, phenyl-4-methylurazole, and phenyl-3-thio-

[1] This Journal, **27**, 118; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1; **39**, 125. Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618.

urazole, in all of which it has been shown by Acree and Brunel[1] that there are probably two or more tautomeric forms whose equilibrium constants are established practically instantaneously under the conditions maintained in the work, Acree[2] and his collaborators have been able to show that the results are not in harmony with the theories of Comstock,[3] Wheeler,[4] Nef,[5] and Michael,[6] but are in accordance with the theory proposed by Acree,[7] namely, that *in all cases in which these tautomeric urazoles give two or more stable isomeric products as the result of a reaction, they do so because they exist in two or more forms in equilibrium, each of which reacts independently, or because one form is changed into stable derivatives through two or more side reactions.* The ratio of the products obtained depends entirely on the equilibrium conditions and the several reaction velocities. The mathematical treatment of this theory has been worked out in detail for the most part[8] and all the experimental results are in harmony with what the theory demands. This theory is not being followed blindly, however; it is used as a working hypothesis and is being subjected to the same rigid scrutiny that was applied to the others. It will be discarded as soon as it has outlived the "day of usefulness" that is the glory of man or theory.

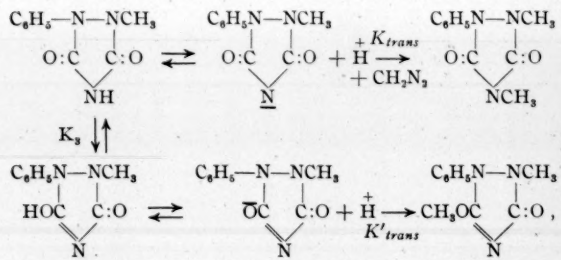
Since, however, all the work up to the present has been done on the metallic salts, it seemed desirable to study the reactions of the urazole acids themselves, the compounds chosen being those that under the conditions studied established the equilibrium practically instantaneously.

This report is confined to the reactions of the diazoalkyls with the urazole acids. The diazoalkyls were chosen as the alkylating agents because (1) they all, with the very important exception of diazopropylene, $CH_2 = CH—CH = N_2$, react *very rapidly* with the urazole acids, and because (2) they yield

[1] Brunel: Diss., Johns Hopkins Univ., 1906.
[2] THIS JOURNAL, **38,** 1; **39,** 125, 226. Ber. d. chem. Ges., **41,** 3199.
[3] Ber. d. chem. Ges., **23,** 2274. THIS JOURNAL, **12,** 493; **13,** 514, 525.
[4] THIS JOURNAL, **21,** 187; **23,** 135; **30,** 28.
[5] Ann. Chem. (Liebig), **266,** 52; **276,** 200; **277,** 59, 83, etc.
[6] J. prakt. Chem., [2] **37,** 469; **45,** 580; **46,** 189; etc.
[7] *Loc. cit.*
[8] THIS JOURNAL, **38,** 1.

a mixture of isomeric esters which can be worked with quantitatively. *It was believed that this would give us a new method for studying the question whether the salts of urazoles have equilibrium constants different from those of the acids, and Mr. E. K. Marshall has now shown that such differences really exist.* As was predicted, these differences are too small to be measured easily by conductivity methods. The diazoalkyl reacts with the urazole acid liberated from the salt by the action of acids, water, alcohol, etc., before it changes into the equilibrium condition, a change that is too small and too rapid to be followed by conductivity measurements.

The salts, when treated with an alkylating agent, have all given a constant ratio of esters in any given series of experiments, but it does not follow that this would be true for the acids.[1] If we consider the following scheme,



[1] Acree showed that 1-phenyl-2-methylurazole and 1-phenyl-4-methylurazole yield with diazomethane *stable* isomeric *N*-esters and *O*-esters. This proves that these urazoles must exist either (A) in only one tautomeric form which reacts with the diazomethane in two (or more) independent side reactions, or (B) in two or more tautomeric forms; in this case (1) each form may react independently with the diazomethane and yield its corresponding ester, or two (or more) esters by side reactions, or (2) one form alone may yield the two esters by side reactions. The probability of (A) can be eliminated by the following evidence: The salts of 1-phenyl-2-methylurazole and 1-phenyl-4-methylurazole exist in two tautomeric forms and the two acids are liberated when a strong mineral acid is added. But it might be thought that one of these tautomeric acids immediately changes into the other and that the acid actually isolated and worked with exists in only one form. But the urazole acids are themselves also weak bases; either tautomeric form of the acid would therefore form a salt with other molecules of itself, which salt would partially rearrange into the other tautomeric salt. Both tautomeric salts are constantly being hydrolyzed, alcoholyzed, etc., into the corresponding two tautomeric acids, which are therefore generally in solution together. Traces of alkalies from glass, etc., could also bring

we readily see that the constancy of ratio between the isomeric esters is only a special case, due either to the fact (1) that the constants for the velocity of establishment of K_3, which is the equilibrium ratio between the molecular enol and keto forms, are very large in comparison with K_{trans}, the velocity constant for the reaction of the keto form with the diazo compound, and K'_{trans}, the corresponding constant for the enol form; or to the fact (2) that, if the constants for the velocity of establishment of K_3 are very small, K'_3, the ratio of the molecular enol and keto forms at the particular time t in question, is approximately equal to $\frac{K_{trans}}{K'_{trans}}$. In K_{trans} and K'_{trans} no consideration is taken of the fact that the acid is ionized or that the reaction may either be ionic or molecular, or both. If α is the percentage of ionization of the keto form of the acid and the reaction is ionic we would have $K_{trans} = \alpha K_{1trans}$, in which K_{1trans} is the real reaction constant.[1] In any case K_{trans} and K'_{trans} are equal to the real reaction constants multiplied by their corresponding factors, the ratio of which factors probably does not change appreciably during the reaction periods measured.

In every other case we would expect the ratio of esters to be dependent on the time. For we have $\frac{c}{c'} = K'_3$ at the time t, and

$$\frac{dc_2}{dt} = \frac{K_{trans}K'_3}{1 + K'_3}(c + c_1 - c_2 - c_3)^2, \text{ and}$$

$$\frac{dc_3}{dt} = \frac{K'_{trans}}{1 + K'_3}(c + c_1 - c_2 - c_3)^2,$$

in which c is the concentration of the practically undissociated keto acid present, c_1 the concentration of the enol acid, c_2 the concentration of the keto ester formed, and c_3 that of the

about such tautomeric changes. We believe that each form of the acid yields (1) the corresponding ester, and not (2) two isomeric esters through side reactions; but we are testing this latter possibility experimentally and practically all of the conclusions arrived at in the following pages can be deduced as readily from one point of view as from the other. We therefore use the former (1) in the following pages for the sake of clearness and convenience, believing it to be nearest the truth.

[1] Ber. d. chem. Ges., **41**, 3212.

enol ester. When equimolecular amounts of acid and diazoalkyl are used, the concentration of the latter is also expressed by $(c + c_1 - c_2 - c_3)$. Dividing and integrating, we obtain, if c_2 and c_3 are zero when $t = 0$,

$$\frac{c_2}{c_3} = \frac{K'_3 K_{trans}}{K'_{trans}}.$$

But if K'_3 is a function of the time, t, then the ratio $\frac{c_2}{c_3}$ would vary accordingly. The reactions between the urazole salts mentioned above and the alkyl halides show most conclusively that the time function of K'_3 need not be considered in the case of these salts. The salts, however, are very different from the acids, being highly ionized and comparable in every way with the salts of strong acids, while the acids themselves are very little ionized,[1] and far less reactive towards alkyl halides. Thus, since the urazole acids react so exceedingly rapidly with diazoalkyl,[2] we might expect different results from some of the urazole acids[3] and then we might get some clue as to the rapidity of establishment of K_3 or its value.

If K'_3 changed very slowly in comparison with the rate of alkylation, then the addition of a small fraction of a molecular equivalent of diazomethane would give a ratio of esters approximately equal to $\frac{cK_{trans}}{c_1 K'_{trans}}$, while the addition of a molecular equivalent would give a ratio approximating K'_3. The addition of different amounts of diazomethane would give a variable ratio, then, unless $K_{trans} = K'_{trans}$, or, in other words, $\frac{c_2}{c_3} = K'_3$.[4] This last possibility can be eliminated by using other diazoalkyls such as diazoethane, -propane, -butane, etc., which give different values of $\frac{c_2}{c_3}$, which would then not be equal to K'_3. On the other hand, if K'_3 is not a function of

[1] THIS JOURNAL, **39**, 126.

[2] Ber. d. chem. Ges., **27**, 1889.

[3] We have now found this to be the case with the tautomeric 1-phenyl-3-oxy-4-phenyl-5-thiolurazole and 1-phenyl-3-hydroxy-4-phenyl-5-thionurazole which change into each other slowly. Dr. Nirdlinger's results will appear soon, and those of Mr. E. P. Doetsch later.

[4] THIS JOURNAL, **38**, 7.

t, when compared with K_{trans} and K'_{trans}, we should expect a constant ratio of esters as in the case of the salts. The experimental evidence shows conclusively that we do get a constant ratio of esters for variable amounts of diazoalkyl used. We must conclude, therefore, that however rapidly the diazoalkyls act with 1-phenyl-2-methylurazole, the various equilibrium constants are established very much more rapidly. Mr. E. K. Marshall is studying these reactions at low temperatures to see if the changes take place slowly enough to be measured under those conditions.

Owing to the fact that the diazoalkyls are decomposed so rapidly by water,[1] it was impossible to use aqueous solutions in studying these reactions. It was hoped that aqueous solutions could be used because Acree and Shadinger[2] have determined the affinity constants of a number of these urazoles in water. An attempt was made to suspend the 1-phenyl-2-methylurazole in water and add a ligroin solution of diazomethane, but only a few milligrams of ester were obtained. The amount was too small to analyze and besides it may have been formed from the small amount of the acid which was dissolved by the ligroin. With an ether solution of diazomethane and an aqueous solution of the urazole acid no better results were obtained. This difficulty with the aqueous solutions, combined with the extreme rapidity of the reaction, made an exact study of its mechanism impossible, but still we have some clues as to its general nature. *Whatever the nature of the reaction between the diazoalkyl and one of the tautomeric forms of the acid, the reaction between it and the other form must be of the same* APPARENT[3] *order.* Otherwise we would not get a constant ratio of esters for variable amounts

[1] von Pechmann: Ber. d. chem. Ges., **27,** 1889.

[2] THIS JOURNAL, **39,** 124.

[3] The possibility that one ester is formed by a bimolecular reaction, for example, and the other ester from the same or another tautomeric form of the acid by a far more complicated but apparently bimolecular reaction, as Julius Meyer (Z. physik. Chem., **66,** 81; **67,** 257) has found in other very interesting cases, seems to be excluded by the fact that *all* diazoalkyls yield ratios of esters which do not vary with different concentrations and different time periods. It would be in only one case in a very large number that *even two* diazoalkyls could behave in such a way, as a large number of constants would be involved in the two sets of reactions yielding the two esters. The two sets of reactions are therefore probably very similar.

of alkylating agent used. For while the theory of side reactions of the same order requires that the ratio of products during any one reaction be constant, no matter what the order of the reactions,[1] since it depends solely on the ratio of the velocity constants, at the same time, even if K'_3 is constant, a changing ratio of products will be obtained when the two reactions are of a different order, since the rates of formation of the two esters will not be changed in the same way. If, for example, the keto ester is formed by a bimolecular reaction and the enol ester by the following trimolecular reaction between the urazole acid and the diazoalkyl, the concentration of which at any moment is designated by $(A - c_2 - c_3)$, we have

$$\frac{dc_2}{dt} = \frac{K_{trans}K_3}{1 + K'_3}(c + c_1 - c_2 - c_3)(A - c_2 - c_3),$$

$$\frac{dc_3}{dt} = \frac{K'_{trans}}{1 + K'_3}(c + c_1 - c_2 - c_3)(A - c_2 - c_3)^2, \text{ and}$$

$$\frac{dc_2}{dc_3} = \frac{K_{trans}K'_3}{K'_{trans}} \cdot \frac{1}{(A - c_2 - c_3)}.$$

On integrating the last equation we would get an expression involving $(A - c_2 - c_3)$. Since K'_3 is a constant the ratio $\frac{c_2}{c_3}$ would then depend on $(A - c_2 - c_3)$ or the concentration of the diazoalkyl, which is a function of t, and $\frac{c_2}{c_3}$ would therefore vary with t. Since we get a constant ratio of esters from those diazoalkyls which react very rapidly, as well as from diazopropylene, which reacts very slowly, we know that the two reactions are of the same apparent order.

There is no experimental evidence from this work as to whether the diazoalkyls form intermediate complex anions or cations. It seems probable that diazomethane is basic in character and would form the complex cation $CH_2N_2\overset{+}{H}$. These complex ions might react with the urazole ions or the urazole molecules; very little is really known about this reaction. It follows from equations (1) and (2), on pages 365, 366,

[1] Acree: THIS JOURNAL, **38**, 1–8. Wegscheider: Z. physik. Chem., **30**, 593.

that $\frac{C_{ei}}{C_{ki}} = K\frac{C_{e\ mol}}{C_{k\ mol}}$. In acid solutions, therefore, there is *always* practically a constant ratio of the ions and also of the molecules of the two tautomeric forms, and the fact that a constant ratio of esters is obtained, even when, as shown by Mr. Marshall, hydrochloric acid is added, does not give any evidence as to whether the ions or the undissociated molecules yield the esters. In the case of diazoacetic ester, which reacts thus,

$$ROOCCH = N_2 + \overset{+}{H} + \overset{-}{Cl} + (H \pm OH) \text{ or } H_2O \longrightarrow ROOCCH_2OH + \overset{+}{H} + \overset{-}{Cl} + N_2,$$

the velocity is dependent upon the concentration of the hydrogen ions and is, according to Bredig and Fraenkel, therefore due to intermediate complex salt and ion formation.[1] Our reactions may or may not be similar, and we shall study the reactions of these urazoles with diazoacetic esters.

This problem also permits us to study the question of abnormal hydrolysis of salts of tautomeric compounds.[2] The hydrolysis of the salts of strong bases and weak acids is expressed by the equation $K_{hyd} = \frac{K_w}{K_{affur}}$, in which K_{hyd} is the hydrolysis constant, K_w the ion product of water, and K_{affur} the affinity constant of the urazole acid. But if there are two tautomeric salts in equilibrium, the affinity constant of the acid is not a simple number and is dependent on the affinity constant of the keto form and on that of the enol form, or other reacting form, whatever its nature, both of which are formed by the hydrolysis of the corresponding salts. Taking the scheme on page 360, we see that the affinity constant of the keto form is

$$K_{affk} = \frac{(C_{ki} \times H)(1 + K_2)}{K_3 \times C_{ur}} \qquad (1),$$

that of the enol form

[1] Ber. d. chem. Ges., **40**, 4015. Bredig: Chemische Kinetik des Diazoessigesters und ihre Anwendungen: Z. physik. Chem., **60**, 202.

[2] Ber. d. chem. Ges., **35**, 210; **39**, 2098; **37**, 2298, 2468; **39**, 1607, 2265. Z. physik. Chem., **47**, 618. For a fuller discussion see Acree: THIS JOURNAL, **38**, 30–41.

$$K_{affe} = \frac{(C_{ei} \times H)(1 + K_3)}{C_{ur}} \qquad (2),$$

and that of the total acid

$$K_{affur} = \frac{(C_{ki} + C_{ei}) \times H}{C_{ur}} = \frac{K_{affe} + K_3 K_{affk}}{1 + K_3} \qquad (3),$$

in which K_{affk} is the affinity constant of the keto form, K_{affe} that of the enol form, K_{affur} that of the total acid, C_{ki} the concentration of the keto ions, C_{ei} that of the enol ions, and H that of the hydrogen ions. C_{ur} is the concentration of the molecular urazole acid, and K_3 has the usual significance. But if the affinity constants of the two forms are different, anything that will disturb K_3 will change the value of K_{affur}. We would then get a new value, K'_{hyd}, for the hydrolysis constant, which would be equal to $\frac{K_w}{K'_{affur}}$, in which K'_{affur} is the new affinity constant of the urazole acid. This could be brought about in certain cases by adding a salt which would not only have a different equilibrium constant, K'_3,[1] but would also introduce a new ratio $C'_{ki} : C'_{ei}$ into the solution. Now we have proved, by the application of the mass law to such a case, that all salts must have a constant ratio of the concentrations of the two anions; namely, that for the acid itself, $C_{ki} : C_{ei}$. Notwithstanding this our experimental results *seem* to indicate that the addition of such a salt changes $C_{ki} : C_{ei}$ and hence K_3. If this is true it may take place because the ordinary formula for the mass law does not hold in the rather concentrated solutions that we use, or because by the addition of the salt we are changing the *medium*, in which the values of K_1, K_2 and K_3, etc., may change. If this is true, then the addition of a diazoalkyl to a solution of 1-phenyl-2-methylurazole containing several molecular amounts of the sodium salt should give an abnormal ratio of esters, since not only the value of K_3 but also the ratio of the ionic forms changes. We actually obtain an increase of *5 per cent.* in the amount of enol ester in the presence of the salt. This proves that there is either an increase in the ratio of the concentration of the

[1] Mr. Marshall and Mr. Doetsch have now shown this to be the case with the tautomeric forms of 1-phenyl-2-methylurazole and 1-phenyl-3-hydroxy-4-phenyl-5-thionurazole.

enol ions to that of the keto ions, or that there is a corresponding change in the ratio of the concentration of the *enol molecular* form to that of the keto molecular form, and these conclusions are beautifully substantiated by Mr. E. K. Marshall's proof that the acid liberated from the sodium salt and alkylated *at once* with diazomethane yields a higher ratio of enol ester to keto ester than does the same acid after it attains its equilibrium. This proves then that there must be a change in the affinity constant of this urazole acid in the presence of its salts—and hence a change in the hydrolysis constant. In the other cases which we are studying, it now appears that some urazole acids will give a *lower* ratio of enol ester to keto ester, and others will hardly have the normal ratio changed, in the presence of the salt. In other words, it seems now that some urazole acids will give a hydrolysis constant which is abnormally high, others a normal hydrolysis constant, and still others an abnormally low hydrolysis constant.

All of the above reactions would necessarily be modified to some extent if the urazole salt causes a catalytic change in the two reaction velocities, or if any other reactions not considered above are found to be taking place. We realize that these reactions may be very complicated and that conclusions can be drawn only tentatively at present. But that the *sodium ions* do not produce this change is shown by the fact that sodium iodide did not cause an appreciable change in the ratio of esters, a difference of only 0.3 per cent. being observed. This is far less than the experimental error. We must yet determine whether urazole ions can effect such catalytic changes. The following table shows the results obtained:

20 cc. 0.0523 Vol. Normal 1-Phenyl-2-methylurazole in Methyl Alcohol and 30 cc. Ethereal Diazoethane Solution.

Conc. diazo sol.	0.0087	0.0174	0.0261	0.0348	
	Per cent. *N*-ester in total product.				Average.
1 - Phenyl - 2 - methylurazole	69.0	67.1	68.4	67.5	68.0
1 - Phenyl - 2 - methylurazole and 3 mols. sodium salt	64.0	64.5	62.3	61.1	63.0
1 - Phenyl - 2 - methylurazole and 3 mols. NaI	68.7	67.2	66.6	68.3	67.7

EXPERIMENTAL.

Phenylurazole.—Phenylurazole was prepared according to the method described by Acree.[1] It melted at 261°–264° without decomposition.

1 - Phenyl - 2 - methylurazole. — The 1 - phenyl - 2 - methylurazole used in this work was made as follows: Twenty grams of phenylurazole were suspended in 200 cc. of alcohol and the theoretical amount of aqueous potassium hydroxide was added. Then about two molecular amounts of methyl iodide were added and the whole mixture was boiled four hours under a return condenser. The solution was evaporated to remove the alcohol and the excess of methyl iodide, and then acidified and filtered. The precipitate was extracted with chloroform to separate the unchanged phenylurazole, which is insoluble. The chloroform solution was filtered and extracted with alkali, which removes the 1-phenyl-2-methyl- and 1-phenyl-3-methoxyurazole and leaves any dialkyl derivative in the chloroform. The alkaline extract was acidified and filtered and the precipitate was evaporated with concentrated hydrochloric acid several times to dryness on a water bath to hydrolyze the methoxy ester. Then the phenyl-2-methylurazole was extracted from the insoluble phenylurazole with chloroform, and the solid obtained by evaporating the chloroform was crystallized from alcohol. From 20 grams of phenylurazole 8.5 grams of 1-phenyl-2-methylurazole melting at 185°–186°, 0.5 gram melting at 175°–178° and a residue of 1.5 grams of esterified product were obtained. The unchanged phenylurazole was recovered.

ON SOME 1-PHENYL-2-METHYL-4-ALKYLURAZOLES.

(BY WM. J. HEAPS.)

As the reactions of 1-phenyl-2-methylurazole are being studied extensively in this laboratory, it was thought desirable to make various 4-alkyl derivatives of it in order to characterize them. The 1-phenyl-2-methylurazole used in this work was made in the usual way and melted sharply at 185°.

[1] THIS JOURNAL, **38**, 56.

1 - Phenyl - 2 - methyl - 4 - ethylurazole. — To 5 grams of dry 1-phenyl-2-methylurazole were added 22.5 cc. of a normal solution of potassium hydroxide and then 60 cc. alcohol and 1.2 molecules of methyl iodide. The mixture was boiled on the water bath under a return condenser for 6 hours, the alcohol evaporated off and the residue evaporated to dryness with hydrochloric acid in order to saponify any *O*-ester present. An excess of alkali was added and the *N*-ester extracted with chloroform and recrystallized from alcohol. It was a white solid soluble in alcohol, ether and chloroform, and melting at 112°. Yield, 2.5 grams.

Hydrolysis.—The ester was hydrolyzed in small tubes with alcoholic hydrochloric acid in the usual way[1] to see if any *O*-ester were present, but only a trace was found mixed with the *N*-ester.

0.1195 gram of ester lost 0.0009 gram, or 0.75 per cent.

Phenyl-2-methyl-4-propylurazole.—This was made from sodium phenyl-2-methylurazole and propyl iodide in the usual way: 2.4 grams of ester melting at 75° were obtained from 5 grams of phenyl-2-methylurazole. The hydrolysis showed the substance to be 99 per cent. pure. Hydrolysis:

0.101 gram of ester lost 0.001 gram, or 1 per cent.

0.1111 gram of ester lost 0.0008 gram, or 0.7 per cent.

Analysis:

0.1764 gram substance gave 0.3997 gram CO_2.

	Calculated for $C_{12}H_{15}O_2N_3$.	Found.
N	61.7	61.8

Phenyl-2-methyl-4-butylurazole.—This was made from sodium phenyl-2-methylurazole and butyl iodide. The ester is a heavy oil and could not be made to solidify, although many different solvents were used. That it was practically freed from the isomeric *O*-ester by the treatment with the alcoholic hydrochloric acid is shown by the following analysis:

Hydrolysis:

0.1143 gram of oil lost 0.0006 gram, or 0.5 per cent.

[1] See page 374.

Phenyl-2-methyl-4-isoamylurazole.—This ester was prepared in the usual way from sodium phenyl-2-methylurazole and isoamyl iodide. Two grams of phenyl-2-methylurazole gave 0.95 gram ester melting at 179°. The ester was soluble in alcohol, ether and chloroform. The treatment with alcoholic hydrochloric acid removed nearly all of the isomeric *O*-ester.

Hydrolysis:

0.1189 gram ester lost 0.0026 gram, or 2 per cent.

ON THE VELOCITY OF ALKYLATION OF THE SODIUM AND SILVER SALTS OF PHENYL-2-METHYLURAZOLE.

It was thought desirable to measure the values of the alkylation constants, and the ratios of esters formed, in the reactions between the salts of 1-phenyl-2-methylurazole and methyl and ethyl iodide, in order to get an indication of its properties and to compare it with 1-phenyl-4-methylurazole.[1] The sodium 1-phenyl-2-methylurazole was made by the method described by Shadinger.[2] The acid suspended in water was carefully neutralized by adding the theoretical amount of acid sodium carbonate and the resulting solution was evaporated on the water bath to dryness, water added and the evaporation to dryness repeated several times. Then the salt was crystallized once from water and dried in an air bath at 115°. It was neutral to phenolphthalein and perfectly white. In making the silver salt the 1-phenyl-2-methylurazole[3] was dissolved in the theoretical amount of potassium hydroxide and one molecular equivalent of silver nitrate was added. The white precipitate formed was filtered off, washed thoroughly with water, then with alcohol and ether, and dried on a porous plate. When pure it was not readily discolored by the light.

The alkylations were carried out as already described.[4] In the case of the silver salt it was impossible to obtain any reaction constants, as the silver iodide seemed to coat the unchanged urazole salt, even when the tubes were shaken con-

[1] Ber. d. chem. Ges., **41**, 3225–3235.
[2] This Journal, **39**, 132.
[3] *Ibid.*, **38**, 59.
[4] Ber. d. chem. Ges., **41**, 5221.

tinuously during the alkylation. The experiments were carried out at 60°.[1] The constants were calculated by the usual bimolecular equation.

Table I.—0.3 Wt. N Sodium Salt of Phenyl-2-methylurazole and 0.3 Vol. N Methyl Iodide at 60°.[2]

t (hours).	*A*.	Total product.	Per cent. *N*-ester.	*AK*.	*AK'* *N*-deriv.	*AK''* *O*-deriv.
1	0.307	0.1890	96.0	1.6	1.53	0.07
2	0.307	0.2399	98.3	1.8	1.77	0.03
3	0.307	0.2616	95.5	1.9	1.81	0.09
4	0.307	0.2627	....	1.9	....	....

Table II.—0.3 Wt. N Silver Salt of Phenyl-2-methylurazole and 0.3 Vol. N Methyl Iodide at 60°.

t (hours).	*A*.	Total product.	Per cent. *N*-deriv.	Per cent. *O*-deriv.
8	0.307	0.0893	51.0	49.0
17.5	0.307	0.0913	52.3	47.7
24	0.307	0.0877	49.5	50.5
28	0.307	0.0935	51.7	48.3

Table III.—0.3 Wt. N Sodium Salt of Phenyl-2-methylurazole and 0.3 Vol. N Ethyl Iodide at 60°.

t (hours).	*A*.	Total product.	Per cent. *N*-ester.	*AK*.	*AK'* *N*-deriv.	*AK''* *O*-deriv.
0.5	0.3285	0.0298	(100.1)	0.199	0.199	...
1	0.3285	0.0607	91.0	0.226	0.205	0.021
2	0.3285	0.0848	91.0	0.174	0.158	0.016
3	0.3285	0.1042	95.8	0.154	0.147	0.007
4	0.3285	0.1144	...	0.133	...	...

Table IV.—0.3 Wt. N Silver Salt of Phenyl-2-methylurazole and 0.3 Vol. N Ethyl Iodide at 60°.

t (hours).	*A*.	Total product.	Per cent. *N*-deriv.	Per cent. *O*-deriv.
10	0.3285	0.0595	11.1	88.9
17.5	0.3285	0.1168	11.0	89.0
23	0.3285	0.1161	10.1	89.9
48	0.3285	0.0960	13.3	86.7

The 1-phenyl-2,4-dimethylurazole obtained from the experiments with methyl iodide melted sharply at 96°,[3] while

[1] For description of the bath see Brunel: Diss., Johns Hopkins Univ., 1906.

[2] Ber. d. chem. Ges., **41**, 3231, 3232.

[3] *Ibid.*, **21**, 1223; **35**, 1563. THIS JOURNAL, **38**, 69.

the 1-phenyl-2-methyl-4-ethylurazole melted at 114°.5.[1] From these experiments we see that this sodium salt is less reactive than the sodium salt of 1-phenyl-4-methylurazole.[2] It gives, however, about the same ratio of esters. When we come to the silver salts we find that while with methyl iodide the ratio of esters is about the same, with ethyl iodide the silver phenyl-2-methylurazole gives much more oxygen ester than the corresponding silver 1-phenyl-4-methylurazole under the same conditions.[2] That the salts of 1-phenyl-2-methylurazole are less reactive is what might be expected from the work of Shadinger[3] on the affinity constants of these acids, the salts of the stronger urazole acids having generally higher alkylation velocities. It has therefore been found that the 4,5-urazole group has a greater tendency to give oxygen derivatives than the 2,3-group.

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZOMETHANE.

The ether used in this work was dried over sodium, the acetone and chloroform over fused calcium chloride and the alcohols over lime, and distilled. Diazomethane was made by the method of von Pechmann.[4] The methylurethane, obtained by the reaction of methylamine on ethyl chlorcarbonate, was treated in ether solution with the gases evolved by the action of nitric acid on arsenious oxide in order to obtain the methylnitrosourethane. According to von Pechmann[5] this substance, as well as the diazomethane, is extremely poisonous. Dr. Nirdlinger found, however, that neither of these substances had any ill effect on the skin, and the diazomethane did not affect his breathing in any way. The alkylations were carried out as follows: One gram of 1-phenyl-2-methylurazole was dissolved in a measuring flask in 100 cc. of the solvent to be used. In the case of ether 0.65 gram was the maximum amount of urazole that could be dissolved. Of this solution 20 cc. were taken for each experiment. The

[1] THIS JOURNAL, **38**, 76.
[2] *Loc. cit.*
[3] THIS JOURNAL, **39**, 126.
[4] Ber. d. chem. Ges., **27**, 1888; **28**, 855, 1624; **29**, 2591; **30**, 646.
[5] *Ibid.*, **27**, 1888.

diazomethane solution was made by pipetting 2 cc. of the methylnitrosourethane into a dry 250 cc. flask and adding 30 cc. of dry ether and 2.2 cc. of a 25 per cent. methyl alcohol solution of potassium hydroxide.[1] Then the ether and diazomethane were distilled over into a receiver containing a small amount of ether to absorb the diazomethane gas, which came over very rapidly at first. The diazomethane solution was then made up to 100 cc. Ten cc. of this solution were transferred to a dry extraction funnel and an excess of a standard ethereal iodine solution added. The excess of the iodine was titrated back with sodium thiosulphate solution, starch being used as an indicator. This gave the strength of the diazomethane solution in cc. of iodine.[2] From a curve, prepared on the basis of this, the amount of diazomethane solution equivalent to 0.2 gram 1-phenyl-2-methylurazole was calculated. Then one-fourth of this amount of diazomethane solution was pipetted into a 100 cc. bottle and sufficient ether to make the solution up to 30 cc. was added. In the next bottle one-half, in the next three-quarters, and in the last, one molecular equivalent of the diazo solution was made up to 30 cc. as above. Usually it took from 20 to 22 cc. of the diazo solution for 0.2 gram of 1-phenyl-2-methylurazole. Twenty cc. of the urazole solution described above was run beneath the ether by means of a pipette and the bottles were shaken. The yellow color of the solutions generally disappeared immediately in all of the bottles; but in some cases a slight yellow color remained in the bottle containing equimolecular amounts of the two solutions. The mixed solvents were then evaporated off, the residue was transferred to an extraction funnel by means of chloroform and then extracted several times with alkali to remove the unchanged acid. Finally the chloroform solution was carefully evaporated off below its boiling point in a weighed dish. After the ester had come to constant weight in a vacuum desiccator, it was

[1] Ber. d. chem. Ges., **28**, 855.

[2] Monats. Chem., **24**, 364. Wegscheider and Gehringer reported that they obtained twice the amount of ester calculated from the iodine used. This does not agree with our experience. Careful experiments have generally shown the ester formed and iodine used to correspond, but there are in some cases apparent discrepancies which we are investigating.

transferred by means of chloroform or ethyl bromide to a small tube drawn out to a capillary at one end. The solvent was then evaporated down to one or two cc. and 5 cc. of a saturated alcoholic hydrochloric acid solution added, and the tube was sealed off. The tube, which had to be handled carefully, was heated 1 hour at 100° and was then cooled and opened. The contents, after being transferred to a separating funnel, were extracted with alkali. This removed the 1-phenyl-2-methylurazole resulting from the hydrolysis of the 1-phenyl-2-methyl-5-methoxyurazole or 1-phenyl-2-methyl-3-methoxyurazole. The chloroform was evaporated off in a weighed dish and the resulting nitrogen ester was weighed. The error of this method is about 3 per cent.[1]

Experiment 1.—20 cc. ether solution containing 0.13 gram of 1-phenyl-2-methylurazole (0.034 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.00568	0.0200	0.0199	(99.5)	(0.5)
0.01136	0.0337	0.0309	91.7	8.3
0.01703	. . . .	. . . .	. . . .	. . .
0.0227	0.1254	0.1136	90.6	9.4

Experiment 2.—20 cc. chloroform solution containing 0.25 gram 1-phenyl-2-methylurazole (0.0654 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0109	0.0928	0.0843	90.8	9.2
0.0218	0.1114	0.1049	94.0	6.0
0.0328	0.2759	0.2563	92.9	7.1
0.0437	0.2735	0.2535	92.7	7.3

Experiment 3.—20 cc. acetone solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0851	0.0764	90.0	10.0
0.0174	0.1850	0.1691	91.3	8.7
0.0261	0.1953	0.1757	89.6	10.4
0.0348	0.2150	0.1958	91.1	8.9

[1] Ber. d. chem. Ges., **41**, 3223.

Experiment 4.—20 cc. ethyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0889	0.0844	94.9	5.1
0.0174	0.1762	0.1632	92.6	7.4
0.0261	0.1976	0.1841	93.1	6.9
0.0348	0.2036	0.1870	92.0	8.0

Experiment 5.—20 cc. ethyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 3 mols. (0.670 gram) sodium 1-phenyl-2-methylurazole and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0910	0.0836	91.8	8.2
0.0174	0.1661	0.1494	90.0	10.0
0.0261	0.2105	0.1904	90.5	9.5
0.0348	0.2190	0.1978	90.3	9.7

Experiment 6.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0676	0.0609	90.4	9.6
0.0174	0.1143	0.1031	90.2	9.8
0.0261	0.1538	0.1378	89.6	10.4
0.0348	0.2136	0.1905	89.2	10.8

Experiment 7.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 3 mols. (0.670 gram) sodium 1-phenyl-2-methylurazole, and 30 cc. ethereal diazomethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.1121	0.0989	88.3	11.7
0.0174	0.1822	0.1628	89.3	10.7
0.0261	0.1786	0.1584	88.7	11.3
0.0348	....	....	....	....

Table V.

Solvent.	Per cent. *N*-ester. 0.25 mol. diazomethane.	0.5 mol. diazomethane.	0.75 mol. diazomethane.	1 mol. diazomethane.
Ether	....	91.7	....	90.6
Chloroform	90.8	(94.0)	92.9	92.7
Acetone	90.0	91.3	89.6	91.0
Ethyl alcohol	(94.9)	92.6	93.1	92.0
Ethyl alcohol and 3 mols. sodium salt	91.8	90.0	90.5	90.3
Methyl alcohol	90.4	90.2	89.6	89.2
Methyl alcohol and 3 mols. sodium salt	88.3	89.3	88.7	....

The 1-phenyl-2,4-dimethylurazole from these experiments melted at 96° and a mixture of this ester and the ester made from sodium 1-phenyl-2-methylurazole and methyl iodide also melted at 96°.

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZOETHANE.

The experiments with diazoethane were carried out in the same way as those with diazomethane. The diazoethane was made from ethylnitrosourethane as described by von Pechmann.[1]

Experiment 1.—20 cc. acetone solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.1054	0.0708	67.2	32.8
0.0174	0.1902	0.1302	68.4	31.6
0.0261	0.1048	0.0734	70.0	30.0
0.0348	0.2199	0.1505	68.4	31.6

Experiment 2.—20 cc. ethyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0741	0.0550	(74.2)	(25.8)
0.0174	0.1393	0.0923	(66.2)	(33.8)
0.0261	0.1730	0.1212	70.0	30.0
0.0348	0.1740	0.1227	70.5	29.5

[1] Ber. d. chem. Ges., **31**, 2643.

Experiment 3.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 N) and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0307	0.0212	69.0	31.0
0.0174	0.0727	0.0488	67.1	32.9
0.0261	0.0763	0.0522	68.4	31.6
0.0348	0.1030	0.0695	67.5	32.5

Experiment 4.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole and 3 mols. (0.670 gram) sodium 1-phenyl-2-methylurazole, and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0862	0.0552	64.0	36.0
0.0174	0.1208	0.0780	64.5	35.5
0.0261	0.1388	0.0864	62.3	37.7
0.0348	0.1707	0.1043	61.1	38.9

Experiment 5.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole and 3 mols. (0.47 gram) sodium iodide, and 30 cc. ethereal diazoethane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0330	0.0227	68.7	31.3
0.0174	0.0409	0.0275	67.2	32.8
0.0261	0.0563	0.0362	66.6	33.4
0.0348	0.0662	0.0452	68.3	31.7

Table VI.

Solvent.	Per cent. *N*-ester. 0.25 mol. diazoethane.	0.5 mol. diazoethane.	0.75 mol. diazoethane.	1 mol. diazoethane.
Acetone	67.2	68.4	70.0	68.4
Ethyl alcohol	....	....	70.0	70.5
Methyl alcohol	69.0	67.1	68.4	67.5
Methyl alcohol and sodium salt	64.0	64.5	62.3	61.1
Methyl alcohol and sodium iodide	68.7	67.2	66.6	68.3

The 1-phenyl-2-methyl-4-ethylurazole melted at 114°.5[1]

[1] THIS JOURNAL, **38**, 76, and page 369 in this article.

and was identical with the ester obtained from sodium 1-phenyl-2-methylurazole and ethyl iodide.

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZOPROPANE.

Propylurethane was made from ethyl chlorcarbonate and propylamine. A one-liter separating funnel was half filled with water and 9.5 grams ethyl chlorcarbonate dissolved in 100 cc. ether were added. Five grams of propylamine diluted with ether were poured in slowly with frequent shaking and then small amounts of caustic potash solution were added, until the water remained alkaline after vigorous shaking. The ether solution was separated, dried, and evaporated and the propylurethane was distilled. It is a colorless liquid boiling at 191°.5–192°.5 under a pressure of 758 mm. The yield was 7 grams, or 72 per cent. of the theoretical. Analysis:

0.3625 gram substance gave 34.68 cc. nitrogen at 762.25 mm. and 27°.

	Calculated for $C_6H_{13}O_2N$.	Found.
N	10.68	10.56

Propylnitrosourethane was obtained by passing nitrous anhydride into an ethereal solution of propylurethane until it became dark green. The ethereal solution was then washed several times with water, then with sodium carbonate solution, and dried, and the ether was distilled off. The propylnitrosourethane was distilled in a vacuum. It is a reddish oil and resembles methylnitrosourethane in all its properties. From 5.8 grams of propylurethane 4.3 grams, or 70 per cent. of the theoretical yield, of a product boiling at 94° (uncorr.) under a pressure of 35 mm., were obtained. Analysis:

0.1239 gram substance gave 20.5 cc. nitrogen at 768.54 mm. and 27°.

	Calculated for $C_6H_{12}O_3N_2$.	Found.
N	17.50	18.15

The solution of diazopropane was made in the usual way from propylnitrosourethane and alcoholic potassium hy-

droxide. It did not distil over as readily as the diazoethane and the ether solution was a deep yellow-brown. It seemed to react as rapidly as diazomethane and -ethane.

Experiment 1.—20 cc. acetone solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazopropane solution.

Conc. diazo. sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	....	....	....	....
0.0174	0.1183	0.0819	69.2	30.8
0.0261	0.1733	0.1190	68.7	31.3
0.0348	0.2257	0.1558	69.0	31.0

Experiment 2.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazopropane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.1063	0.0628	59.1	40.9
0.0174	0.1067	0.0635	59.5	40.5
0.0261	0.1148	0.0657	57.2	42.8
0.0261	0.1186	0.0715	60.3	39.7
0.0348	0.1080	0.0643	58.6	41.4
0.0348	0.1370	0.0824	60.1	39.9
0.0348	0.1078	0.0629	58.3	41.7

Table VII.

	Per cent. *N*-ester.			
Solvent.	0.25 mol. diazo-propane.	0.5 mol. diazo-propane.	0.75 mol. diazo-propane.	1 mol. diazo-propane.
Acetone	....	69.2	68.7	69.0
Methyl alcohol	59.1	59.5	58.8[1]	59.0[2]

The 1-phenyl-2-methyl-4-propylurazole melted at 81°–82° and was in every way identical with the ester obtained from sodium 1-phenyl-2-methylurazole and *n*-propyl iodide.[3] This is especially interesting since we have thus eliminated the

[1] Average of two ratios.
[2] Average of three ratios.
[3] See page 369.

possibility of obtaining an isopropyl ester also. For diazopropane may have the structure

$$CH_3CH\underset{N_2}{\diagup\diagdown}CH_2 \text{ or } CH_3CH_2CHN_2.$$

If the first formula were correct we would expect, from the general behavior of such compounds, some isopropyl ester to be formed.

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZOBUTANE.

Butylurethane was made in exactly the same way as propylurethane. It is a colorless liquid boiling at 208°–211° (uncorr.) at 770 mm. From 6 grams butylamine 10 grams pure product, or 83 per cent. of the theoretical yield, were obtained.

Butylnitrosourethane was also made in the same way as propylnitrosourethane. It was more viscous than the propyl compound and could not be distilled even in a vacuum; consequently no further attempt was made to purify it. It decomposed violently at its boiling point.

The diazobutane made from the unpurified butylnitrosourethane was similar to the diazo compounds described before. It evidently is a liquid boiling at a slightly higher temperature than ether, for it did not begin to distil over until most of the ether had already collected in the receiver. The solution was somewhat darker in color than the diazopropane solution. It did not seem to have as disagreeable an odor as diazomethane.

Experiment 1.—20 cc. acetone solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazobutane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0934	0.0597	63.9	36.1
0.0174	0.2048	....	....	....
0.0261	0.2379	0.1508	63.4	36.6
0.0348	0.2421	0.1537	63.5	36.5
0.0348	0.2326	0.1489	63.9	36.1
0.0348	0.2259	0.1430	63.3	36.6
0.0348	0.2090	0.1319	63.1	36.9

Experiment 2.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 vol. N) and 30 cc. ethereal diazobutane solution.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	0.0352	0.0190	54.0	46.0
0.0174	0.0740	0.0402	54.3	45.7
0.0261	0.0948	0.0510	53.8	46.2
0.0348	0.1587	0.0889	56.0	44.0
0.0348	0.1933	0.1072	55.4	44.5

Table VIII.

	Per cent. *N*-ester.			
Solvent.	0.25 mol. diazo-butane.	0.5 mol. diazo-butane.	0.75 mol. diazo-butane.	1 mol. diazo-butane.
Acetone	63.9	63.4	63.5	63.4[1]
Methyl alcohol	54.0	54.3	53.8	55.7[2]

The 1-phenyl-2-methyl-4-butylurazole was obtained as an oil which did not crystallize. The compound made from the sodium salt and butyl iodide is also an oil.[3]

ALKYLATIONS OF 1-PHENYL-2-METHYLURAZOLE WITH DIAZOPROPYLENE.

Allylurethane was made in the usual way from allylamine and ethyl chlorcarbonate. From 5 grams of allylamine, 7.5 grams of a colorless oil boiling at 194°.5–195° (uncorr.) under a pressure of 768 mm. were obtained. Yield, 66 per cent. of the theoretical. Analysis:

0.2487 gram substance gave 24.60 cc. nitrogen at 24° and 755.8 mm.

	Calculated for $C_6H_{11}O_2N$.	Found.
N	10.85	11.00

Allylnitrosourethane was made in the same way as the other nitrosourethanes. It is a reddish oil which decomposes when distilled in a vacuum and so no attempt was made to purify it by distillation.

The ether solution of diazopropylene had a deep wine color instead of the usual yellow color of the other diazo solutions.

[1] Average from four experiments.

[2] Average from two experiments.

[3] See page 369.

The diazopropylene acted on the 1-phenyl-2-methylurazole very slowly, several hours being necessary to discharge the color completely. The amount of ester formed in any one case was very small, as the following experiments show:

Experiment 1.—20 cc. methyl alcohol solution containing 0.20 gram 1-phenyl-2-methylurazole (0.0523 volume N) and 30 cc. of ethereal diazopropylene.

Conc. diazo sol. Vol. N.	Weight of total product.	Weight of *N*-ester.	Per cent. *N*-ester.	Per cent. *O*-ester.
0.0087	....	....	....	....
0.0174	0.0288	0.0194	67.3	32.7
0.0261	0.0368	0.0246	66.8	33.2
0.0348	0.0135	0.0091	67.4	32.6
0.0348	0.0120	0.0079	65.8	34.2

The 1-phenyl-2-methyl-4-allylurazole melts at 61°–64°. The compound was obtained also by the action of allyl iodide on the sodium salt of 1-phenyl-2-methylurazole in alcoholic solution. It melted after crystallization from alcohol at 62°–64° and at 61°–64° when mixed with a sample obtained in the above experiment.

Table IX.—Summary of Experiments in Methyl Alcohol-Ether.

	Per cent. *N*-ester.			
Diazoalkyl.	0.25 mol. diazo-alkyl.	0.5 mol. diazo-alkyl.	0.75 mol. diazo-alkyl.	1 mol. diazo-alkyl.
Diazomethane	90.4	90.2	89.6	89.2
Diazoethane	69.0	67.1	68.4	67.5
Diazoethane + sodium salt	64.0	64.5	52.3	61.1
Diazoethane + sodium iodide	68.7	67.2	66.6	68.3
Diazopropane	59.1	59.5	58.8[1]	59.0[1]
Diazobutane	54.0	54.3	53.8	55.7[1]
Diazopropylene	....	67.3	66.8	66.6[1]

Table X.—Summary of Experiments in Acetone-Ether.

	Per cent. *N*-ester.			
Diazoalkyl.	0.25 mol. diazo-alkyl.	0.5 mol. diazo-alkyl.	0.75 mol. diazo-alkyl.	1 mol. diazo-alkyl.
Diazomethane	90.0	91.3	89.6	91.1
Diazoethane	67.2	68.4	70.0	68.4
Diazopropane	....	69.2	68.7	69.0
Diazobutane	63.9	....	63.4	63.4[2]

[1] Average from two or more experiments.

[2] Average of two or more ratios.

Table XI.—Summary of Experiments in Ethyl Alcohol-Ether.

Diazoalkyl.	Per cent. *N*-ester. 0.25 mol. diazoalkyl.	0.5 mol. diazoalkyl.	0.75 mol. diazoalkyl.	1 mol. diazoalkyl.
Diazomethane	94.9	92.6	93.1	92.0
Diazomethane + sodium salt	91.8	90.0	90.5	90.3
Diazoethane	....	....	70.0	70.5

Table XII.—Summary of Experiments in Chloroform-Ether.

Diazoalkyl.	Per cent. *N*-ester. 0.25 mol. diazoalkyl.	0.5 mol. diazoalkyl.	0.75 mol. diazoalkyl.	1 mol. diazoalkyl.
Diazomethane	90.8	94.0	92.9	92.7

Table XIII.—Summary of Experiments in Ether-Ether.

Diazoalkyl.	Per cent. *N*-ester. 0.25 mol. diazoalkyl.	0.5 mol. diazoalkyl.	0.75 mol. diazoalkyl.	1 mol. diazoalkyl.
Diazomethane	....	91.7	....	90.6

The above tables show conclusively that constant ratios are obtained for varying amounts of diazoalkyl. The maximum variation in any one series is not over 5 per cent. and the average variation is only about 1.5 per cent., or well within the limit of experimental error. Another fact that is noticed at once is the increase in the amount of oxygen ester with increase in weight of the alkyl group. When we change from diazomethane to diazoethane, in the methyl alcohol solutions, we have a change of 20 per cent. in the ratio of esters, a change of 10 per cent. when we change from diazoethane to diazopropane, and then only a change of 5 per cent. when diazobutane is used. In the experiments in acetone there is about the same difference in the diazomethane and -ethane series. It seems peculiar that here diazoethane and -propane should give about the same ratios. There is, however, a drop of about 5 per cent. in the ratios obtained when diazobutane is used instead of diazopropane. Taken all together, the experiments show conclusively that, as rapid as the alkylations are, K_3 is established so rapidly that it need not be considered to vary with different time periods.

CONCLUSIONS.

1. The conditions affecting the constancy of the ratio of products obtained from a tautomeric substance have been discussed.

2. 1-Phenyl-2-methylurazole has been alkylated with varying molecular proportions of different diazoalkyls and in all cases, for any one series of experiments, a constant ratio of esters has been obtained. This shows conclusively that the constants for the velocity of rearrangement of the two forms of 1-phenyl-2-methylurazole are very large in comparison with K_{trans} and K'_{trans}, or, in other words, K_3 is maintained constant during the alkylation.

3. 1-Phenyl-2-methylurazole and a given diazoalkyl give different ratios of esters in different solvents.

4. 1-Phenyl-2-methylurazole and different diazoalkyls give different ratios of esters in the same solvent.

5. Evidence has been given to show how we may have abnormal hydrolysis of the sodium salt of 1-phenyl-2-methylurazole. In the presence of sodium 1-phenyl-2-methylurazole the 1-phenyl-2-methylurazole gives with diazomethane and with diazoethane ratios of esters which are different from the ratios obtained when no sodium salt is present. This leads us to the conclusion that the equilibrium point of the two (or more) tautomeric forms of the sodium salt may be different from that of the two tautomeric forms of the acid, and hence gives a possible explanation of abnormal hydrolysis. These conclusions have been further strengthened by the work of Mr. E. K. Marshall, who has attacked this problem by more direct methods.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, JUNE 1, 1909.

OBITUARIES.

FRIEDRICH KOHLRAUSCH.

Friedrich Kohlrausch, who died suddenly on January 17th, was born at Rinteln on October 14, 1840. He received his early schooling at Rinteln, Kessel-Marburg and Erlangen, and then studied at Göttingen and Erlangen, obtaining his

doctor's degree at the latter university in 1863. He was assistant for a short time at the Göttingen observatory and from 1864 to 1866 was privatdozent of the Physikalischer Verein at Frankfort. Weber having offered him an assistantship, he returned to Göttingen and in the following year was made Professor Extraordinarius. During the four years he remained here, he was not only actively engaged in research work, but succeeded in establishing experimental physics as a branch of the University instruction. It was during this period that his great work on the conductivity of electrolytes was begun; the first record of the use of the alternating current in the study of this problem is dated May 19, 1868. In 1870 he accepted a call to the Zürich Polytechnic Institute, but the following year he went to Darmstadt. In 1875 he succeeded Kundt at Würzburg and again in 1888 at Strassburg when Kundt was called to Berlin. In 1895, on the death of Helmholtz, Kohlrausch was elected president of the Physikalisch-technische Reichsanstalt, and remained at its head till 1905, when ill health compelled him to retire. In 1900 he had been made honorary professor in the University of Berlin and in 1908 the Deutsche Bunsen-Gesellschaft awarded him its first Bunsen medal. The last five years of his life were spent in the quietude of his home at Marburg and at Jugenheim, but he continued his investigations with unabated vigor to the very last.

His greatest work is, of course, the investigation on the conductivity of electrolytes, which proved so fruitful in his hands. We need only mention the discovery of the law of the independent migration of ions, the bridge and telephone method of measuring conductivities, the determination of the conductivity and dissociation constant of pure water, the method for the determination of the solubility of difficultly soluble substances from their conductivity, etc. Of less interest to chemists, but marked by no less skill, resourcefulness and deep insight are his investigations on terrestrial magnetism, elasticity, heat and electrical conduction. As a teacher, his influence has become widely felt, and his book, "Leitfaden der praktischen Physik," the eleventh edition of which was published just before his death, is probably used, at one time or other, by every student of physics in Germany and by many outside of Germany.

WILLARD BRADLEY RISING.

The death of Professor Willard Bradley Rising was announced February 9th. Prof. Rising was born at Mechlenburg, N. Y., on September 26, 1839. He attended Hamilton

College, New York, from which he graduated in 1864. After receiving the degree of M.E. from the University of Michigan in 1867 he taught two years at the then College of California and then went to Germany, where he obtained his doctorate from Heidelberg in 1871. He studied under Hofmann at Berlin for a time and in 1872 was appointed to the chair of chemistry at the University of California, a position which he held without interruption till his death. Since 1885 he had been state analyst of California and for several years was consulting analyst of the State Board of Viticulture, carrying out investigations on the chemistry of wine. In his capacity as consulting analyst of a large powder company he has contributed also to the chemistry of explosives.

REVIEWS.

OUTLINES OF CHEMISTRY. BY LOUIS KAHLENBERG, PH.D., Professor of Chemistry and Director of the Course in Chemistry in the University of Wisconsin. New York: The Macmillan Company. 1909. pp. xix + 548. Price, $2.60.

The fact that he has more than six hundred students under his instruction amply justifies the author in preparing a new text-book for college students. In his position it is desirable that he should satisfy his own views of what should be taught, and how it should be done.

The book is without doubt a very creditable piece of work. The facts and theories are, in general, well selected and presented. An important feature is the emphasis put upon technical applications and processes, which include some of the most recent developments in applied chemistry. It may be observed that the descriptive matter appears to be rather more extensive than is usual in books of this class, while the theory is perhaps somewhat less fully treated than is commonly the case. As a whole, the book may be regarded as presenting a course sufficiently extensive for the average college student.

It is not to be expected that any book will be perfect, but attention may be called to some metallurgical weaknesses which this book exhibits, as is the case with practically all of our text-books on general chemistry. For instance, the use of superheated steam in the Parke's process is here described as applied to the wrong material. The relationship between cast iron and steel is described in a way that is misleading, for it would be inferred that graphite crystallizes out from steel on annealing, while the hardening of steel by

quenching and the chilling of gray cast iron in casting appear to be viewed as identical processes. The characterization of gray and white cast iron as being produced, respectively, by the very slow and the rapid cooling of "cast iron" is entirely wrong, except as far as it applies to the "chilling" of gray iron.

The feature of this book which is likely to attract the most attention is the author's well-known attitude in rejecting as untenable the ionic theory of Arrhenius, and his antagonism towards van't Hoff's application of the laws of gases to solutions. In this attitude he stands practically alone among the present generation of chemists. This feature, however, may be considered as of minor importance, for it must be admitted that he gives a fair discussion of the views which he rejects, and it is quite possible that some moderate adherents of the ionic theory will prefer this treatment of it to its too enthusiastic employment. HORACE L. WELLS.

HEAT ENERGY AND FUELS, PYROMETRY, COMBUSTION ANALYSIS OF FUELS AND MANUFACTURE OF CHARCOAL, COKE AND FUEL GAS. By HANS V. JÜPTNER, Professor Imperial Royal and Technical Institute, Vienna. Translated by OSKAR NAGEL, PH.D. New York: McGraw Publishing Co. 1908. pp. v + 305. Price, $3.

The author treats the subject of chemical technology in four volumes and divides it into (1) chemical technology of energy; (2) chemical technology of materials. The present volume is the first one of the series and deals with the first subject. The English translation of this book is a welcome addition as it brings to our attention a valuable work on the subject of fuels. It contains three hundred pages and, exclusive of the introduction, is divided into twenty-three chapters, as follows: Measurement of High Temperatures, Pyrometry (continued), Pyrometry (conclusion), Combustion Heat and Its Determination, Direct Methods for Determining the Combustion Heat, Incomplete Combustion, Combustion Temperature, Fuels (in general), Wood, Fossil Solid Fuels (in general), Peat, Brown Coal, Bituminous and Anthracite Coals, Artificial Solid Fuels, Charcoal, Peat Coal, Coke and Briquettes, Coking Apparatus, Liquid Fuels, Gaseous Fuels, Producer Gas, Water Gas, Dowson Gas, Blast Furnace Gas and Regenerated Combustion Gases, Apparatus for the Production of Fuel Gases.

This book is intended for use in universities and engineering schools as well as for practicing engineers, as the subject is treated both theoretically and practically. It is made specially valuable because of the large amount of tabulated

data on most of the subjects discussed. Much of this material is not readily accessible and is presented here in convenient form and for this reason the book will commend itself to the practising engineer.

The chapters on pyrometry and heat of combustion are very comprehensive and it may be questioned whether in these chapters certain inaccurate methods might not have been treated more briefly to advantage.

The reviewer would like to call attention to the table on page 243, giving the composition of Pennsylvania natural gas as follows:

Methane	67 per cent.	Ethylene	1 per cent.
Hydrogen	22 per cent.	Carbon dioxide	0.6 per cent.
Nitrogen	3 per cent.	Carbon monoxide	0.6 per cent.
Ethane	5 per cent.		

The most accurate analyses of natural gas around Pittsburg show it to be composed almost entirely of the lower paraffins and nitrogen. It contains no free hydrogen or carbon monoxide and only traces of carbon dioxide. The book will undoubtedly be of great use to students and especially useful to the practical worker. J. C. W. FRAZER.

THE CHEMICAL ANALYSIS OF IRON. A Complete Account of All the Best Known Methods for the Analysis of Iron, Steel, Pig Iron, Iron Ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Producer Gases. By ANDREW ALEXANDER BLAIR. Seventh Edition. Philadelphia and London: J. B. Lippincott Co. 1908. pp. xix + 334. Price, $4.

That this book is in demand and authoritative is shown by the rapidity with which it has passed through its various editions. This edition contains as new matter a method for the separation of vanadium, molybdenum, chromium, and nickel in steel, the volumetric cyanide process for nickel, and some improvements in the methods for gas analysis. In all other respects it remains the same and the best of its class.

To the reviewer, who has used the book since the second edition appeared, it has always been a matter of surprise that the author has not made more of an attempt to make the book one which could be used as a text for students. In very few cases does the author illustrate clearly or at all the principles involved in the methods. It is essentially a statement of details, and frequently the student, and in some cases the average chemist, is lost in a maze of detailed facts. The reviewer has particularly in mind the acetate method for phosphorus. The lack of principle is again shown on page

100 where the author gives an example of the conversion of a potassium permanganate solution, standardized against iron, into its value in terms of phosphorus. To a teacher trying to instil principles this is hopeless, and to any one knowing anything of the significance of figures or precision of measurements, ludicrous. Other cases might be cited.

In a new edition the book could be pruned advantageously. It contains some antiquated methods, such as some of the methods for carbon, which are of importance only from the historical point of view. H. F.

METALLOGRAPHIE. Ein ausführliches Lehr- und Handbuch der Konstitution und der physikalischen, chemischen and technischen Eigenschaften der Metalle und metallischen Legierungen. Von DR. W. GUERTLER, Privatdozent an der Königl. Technischen Hochschule zu Berlin. Erster Band: Die Konstitution. Heft I. Berlin: Gebrüder Bornträger. pp. 80. 1909. Price, M. 4.20.

PHYSIKALISCHE CHEMIE DER METALLE. Sechs Vorträge über die wissenschaftlichen Grundlägen der Metallurgie. Von DR. RUDOLPH SCHENCK, Professor der physikalischen Chemie an der Königl. Technischen Hochschule zu Aachen. Halle: Wilhelm Knapp. 1909. pp. 187. Price, M. 7.00.

LEÇONS SUR LES ALLIAGES MÉTALLIQUES. PAR J. CAVALIER, Professeur Honoraire à la Faculté des Sciènces de l'Université de Rennes. Paris: Vuibert et Nony. 1909. pp. xix + 466.

METALLOGRAFIA, APPLICATA AI PRODUTTI SIDERURGICI. UMBERTO SAVOIA. Assistente di Metallurgia nel R. Instituto Tecnico Superiare di Milano. Milano: Ulrico Hoepli. 1909. pp. xvi + 205. Price, £3.50.

The rapidly growing importance of the subject of Metallography is shown in the recent publication of many books upon various phases of the subject. The accumulation of data has recently been very rapid, and much of this material is now being collected in book form. The subject has been slow in developing when we consider that the scientific foundations were laid by Sarby as early as 1864. Previous to this time there was a vast number of isolated facts, but the methods which were employed in the study of metals and alloys were so crude that rapid development could not have been expected. With the introduction of physico-chemical methods in the study of binary mixtures, and the application of the phase rule, this hitherto chaotic field has been extensively worked, and a new science has been established. By means of the thermocouple and the microscope a science has been founded in which accurate facts replace mere suppositions, and by which such complicated alloys as steel, the brasses and bronzes may be satisfactorily explained.

Dr. Guertler has planned a comprehensive treatise on

Metallography, and proposes to treat of the physical, chemical and technical sides of the subject. In this volume, which deals almost exclusively with the theoretical part of the subject, he discusses the constitution of binary alloys. He reviews the early development of the science, considers the thermal equilibrium diagrams from the point of view of the phase rule, and discusses in detail the subject of solid solutions and compounds. As types of solid solutions, the author gives a detailed discussion of the cooling curves of the manganese-iron, iron-cobalt, and nickel-cobalt alloys, and these will probably be followed by similar examples in the next volumes.

The book is distinctly of an advanced type and will be difficult reading to all except those having had some training in physical chemistry. It will, however, be a very valuable addition to the subject of Metallography, and it is sure to be authoritative. The printing is excellent and the marginal notes very useful. It is sincerely hoped that the succeeding volumes will follow quickly.

Of an entirely different character is the book by Dr. R. Schenck, in which he also treats of the constitution of alloys, but he uses this as a means of preparing his reader for broader problems in equilibrium phenomena. The book consists primarily of a course of six lectures serving as a physico-chemical introduction to the study of metallurgy. The author discusses the physical changes of the metals, the theories of metallic solutions, and the thermal equilibrium diagrams of binary and ternary metallic mixtures. In the application of the theories, the author discusses briefly some binary alloys, and more fully the iron-carbon alloys, and alloys of metals with the nonmetals, such as Cu-Cu_2O, Cu-Cu_2S, Fe-FeS, Pb-PbS, Ni-NiS, Fe-Fe_3P, and some double sulphides. Three chapters are devoted especially to metallurgical reactions such as oxidation and reduction and the equilibrium between various metals and oxygen, or sulphur. Especially important to those interested in the metallurgy of iron is the application of the phase rule in explaining the equilibrium in the system iron, carbon, oxygen. Similar application is made to nonferrous metallurgy.

The book is an excellent treatise on the principles upon which the science of metallurgy is founded. It is concise, clear, well illustrated with diagrams, tables, and photomicrographs.

The book by Professor Cavalier is an exhaustive treatise on the physical and chemical properties of metals and their

alloys, and to any one interested in the properties of metals it will furnish an excellent guide to the theoretical and practical sides of the subject. The author describes the physical properties of the industrially important metals, such as strengh, malleability, hardness, electrical conductivity, magnetism, thermo-electric properties, etc., and the methods for determining these values. The various forms of furnaces, including the recently developed electrical furnaces, are discussed with sufficient detail to give a fair idea of their use. The subject of pyrometry is adequately dealt with, and the author describes some of the various forms of apparatus for measuring high temperatures. The technique of mechanical testing and microscopic metallography is given.

In regard to the more theoretical side of the subject, the author discusses the commercially important binary alloys from the point of view of the phase rule, and with the brasses, bronzes, and bearing metals much technical information is also given. Almost 100 pages of the book are devoted to the consideration of iron and its alloys with carbon, manganese, nickel, chromium, etc., and to the special alloy steels. This part of the book is replete with the most recent information and is an excellent compilation of much widely scattered material.

As a whole, the book deserves much praise, and should be of value to the metallurgist and testing engineer. Many references are given throughout the text, but the book would be of much greater value if the references were more complete.

The book by Savoia is a concise and practical discussion of the principle and technique of the metallography of steel and iron. It discusses briefly the history of the science, the preparation, polishing and etching of specimens; and more fully the structural constituents of iron, iron-carbon alloys, nickel and chrome-nickel alloy, and the various classes of cast irons. The book is excellently illustrated with a large number of photomicrographs, of which there is some unnecessary duplication. The book should be of considerable value to the Italian engineer and metallurgist. H. F.

ANLEITUNG ZUM EXPERIMENTIEREN IN DER VORLESUNG ÜBER ORGANISCHE CHEMIE. Von DR. HANS RUPE, A. O. Professor an der Universität Basel. Mit 30 in den Text eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1909. S. x + 130. Preis: geheftet, M. 4.50; geb., M. 5.40.

This excellent book is presented to organic chemists as a guide for lecture experiments, of which certainly too few are given in America, even to beginners, in the organic field. The

freshman is dazzled with the illumination of the metals and non-metals through lecture-table pyrotechnics, but when he comes later to the far more abstruse problems of carbon chemistry, he is left in the utter darkness of his own efforts at enlightenment. The beginner in organic chemistry needs instructive and impressive lecture-table experiments *and* the usual laboratory course just as much as he did in the inorganic work.

The author acknowledges that, on account of his love for the beauty of the experiments in the aliphatic series, he has through neglect treated the benzene series very much like a mother-in-law. Nevertheless, besides the large number of instructive experiments with aliphatic compounds, he gives a good list of preparations of aromatic compounds. After all, chemists see no very sharp dividing line between the properties of the aliphatic and the aromatic compounds.

The most striking experiments in the benzene series are those involving the dyes, and Professor Rupe has treated the preparation and properties of phenolphthalein, fluorescein, eosin, Congo red, fuchsine, alizarin and indigo very fully.

S. F. Acree.